THE THERMAL DECOMPOSTION OF DIBENZYL

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A Thesis Submitted for the Degree of PhD
at the
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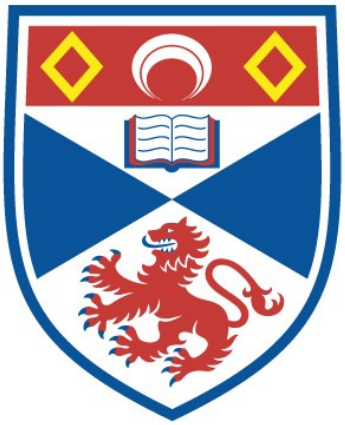

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THE THERMAL DECOMPOSITION OF DIBENZYL

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ROBERT NEILSON PITTILO, B.Sc.,

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mo 2107

DECLARATION

I hereby declare the following Thesis to be a record of results of experiments carried out by me and furthermore that the Thesis is my own composition and has not been previously presented in application for a Higher Degree.

The investigations were carried out in the Chemical Research Laboratories of the United College under the direction of Doctor Charles Horrex.

[redacted]

UNIVERSITY CAREER

I entered the United College of St. Andrews in October 1947, receiving a Second Class Honours Degree in Chemistry in 1951.

The researches described in this Thesis were carried out under the direction of Doctor Charles Horrex in the United College, within the period September 1951 to September 1954.

CERTIFICATE

I hereby certify that Mr. Robert Neilson Pittilo, B.Sc., has spent nine terms at Research Work under my direction, that he has fulfilled the conditions of Ordinance No.16 (St. Andrews) and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research.

ACKNOWLEDGEMENTS

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INTRODUCTION

General Introduction

The present research is concerned with a topic which has received some previous experimental treatment (1). The results of that investigation show several anomalies, and, in view of the current interest in benzyl radicals and their reactions, further research into the problem was considered necessary.

The previous investigators stated that the decomposition followed a first order law with a rate constant given by $k(sec.^{-1}) = 10^{9.29} e^{(-48,000/RT)}$. They postulated as the rate determining step an initial dissociation to benzyl radicals followed by a rapid conversion of these to toluene by hydrogen abstraction reactions. The most outstanding peculiarity of this is the value of $10^{9.29} sec.^{-1}$ obtained for the pre-exponential factor in the rate equation in place of $10^{13} sec.^{-1}$ which is the normal value for unimolecular reactions. The postulate of rapid reaction of the benzyl radicals to form toluene is also strange, as these radicals are usually regarded as being very stable (2) and show a strong tendency to dimerise rather than to take part in side reactions.

In spite of these objections it must be noted that

the activation energy of 46 k.cal./mole. is in excellent agreement with the value expected for the bond dissociation energy of the central C - C bond based on the value, current at that time, for the heat of formation of the benzyl radical (2).

Horrex and Miles were greatly handicapped by analytical difficulties. Facilities for accurate analysis of mixtures of benzene, toluene, styrene and stilbene, the main reaction products, were not available, and the concentrations of the resultants could only be estimated to within 20%. For the present research, there was available an ultraviolet spectrophotometer and a mass spectrometer, although, for the latter, considerable sample handling problems and inconsistencies of response had to be faced before accurate work could be undertaken. However, these facilities eventually made more feasible the analysis of the small amounts of products available.

The initial objectives of the work can be summarised as follows:-

(a) To check the evidence on the nature of the decomposition and its extent;

(b) to check the kinetic equation for the reaction and the dependence of the rate constants on temperature.

In particular it was thought that the anomalous temperature independent factor might be explained most readily if the reaction was not in fact first order, and some step other than the initial dissociation to benzyl radicals determined the rate. It was also conceivable that the postulate of a free radical mechanism could be in error, and some reaction path might be operative which does not involve radicals.

While the research was in progress, a new and substantially different value was suggested for the heat of formation of the benzyl radical (3) and a criticism of the evidence for the previous value was published (34). The import of these is discussed in detail in later sections of the thesis, but it is evident that the correspondence of the observed dissociation energy of Morrex and Miles with that expected for the central C - C bond would be eliminated by a revision of the heat of formation of the benzyl radical. Such a revision would in fact destroy the main point in favour of their kinetic data.

Bond Dissociation Energies and their Determination

This is a subject which has received considerable treatment in the literature in the past few years, and several comprehensive reviews exist (4), (5). Consequent-

ly the treatment here has been limited to approaches which have some direct bearing on the topic under discussion.

Definition

The term Bond Dissociation Energy, as used in this thesis can be defined as the endothermicity of the reaction

$$R_1R_2 \longrightarrow R_1 + R_2 - D(R_1 - R_2) \text{ k.cal./mole.}$$

For the purposes of accurate definition the process should occur at $0^{\circ}K.$ with reactant and resultants in the gas phase, and products in their ground states.

From the point of view of scientific investigation, the dissociation has to be brought about under conditions where energy is supplied to the molecule in a controlled fashion, and the methods used can be subdivided according to the form in which the energy is contributed.

(1) Thermal Methods in which the energy is supplied by raising the temperature of the system.

(2) Photochemical Methods where radiant energy is absorbed by the reacting species or is transferred to it by some other absorbing substance.

(3) Electron Impact Methods which employ the kinetic energy of fast moving electrons.

The present research has been concerned mainly with the use of thermal methods but photochemical techniques

have also been attempted, and certain electron impact data included in the discussion. As a result, it is appropriate that some general account of these techniques should be given.

Thermal Methods

(a) The Chemical Equilibrium Method

This technique is based on the measurement, at various temperatures, of the equilibrium constants for a reaction of the type:-

$$R_1 \cdot R_2 \longleftrightarrow R_1 \cdot + R_2 \cdot$$

and yields the heat of dissociation of the molecule by application of the equation $\frac{d}{dT} \ln . K_{eq.} = \triangle H / RT^2$

A known amount of the compound is introduced into a reaction vessel at a suitable temperature, allowed to reach equilibrium, and the degree of dissociation determined by manometric, colorimetric, magnetic, or other techniques.

To attain a satisfactory degree of accuracy, a high percentage dissociation is a requisite, and hence high temperatures or low pressures must be employed. The latter condition presents the problem of adsorption on the walls of the reaction vessel, a factor which can seriously affect the results. The former increases the possibility of irreversible side reactions.

The method has been successfully employed (for example (6), (7), (8)) for the investigation of reactions of the type $X_2 \longleftrightarrow 2X.$ where X_2 is a diatomic molecule resulting in the formation of atoms which can only recombine, and cannot take part in undesirable side reactions. An exceedingly accurate investigation of the reaction $I_2 \longleftrightarrow 2I.$ has been carried out by Perlman & Rollefson, (64) who, by use of a very sensitive manometric technique, obtained a value of 35.514 ± 0.030 k.cal./mole for the bond dissociation energy, which is remarkably close to the best spectroscopic value.

For a complex molecule of the type R_2, R. being a radical, the method is less useful as various secondary processes such as

(a) disproportionation of radicals

$$R. + R. \longrightarrow M_1 + M_2$$

(b) reactions between radicals and molecules

$$R. + R_2 \longrightarrow M_3 + R'$$

(c) further decomposition of radicals

$$R. \longrightarrow R'' + M$$

can occur.

As such processes are more likely at high temperatures, the method is generally applicable only to molecules in which the R-R bond is exceedingly weak

and the radical R. very stable and inert with respect to R_2.

A suitable example of such a process is the investigation by colorimetry (9) and magnetic susceptibility (10) of the dissociation of hexaphenyl ethane.

$$(Ph.)_3C\text{-}C(Ph.)_3 \longrightarrow 2(Ph.)_3C.$$

Both methods gave a value of 11.3 ± 1 k.cal./mole for the heat of dissociation for this reaction.

The method is included as it was considered by Norrox and Miles (1) that the available evidence on the stability of benzyl radicals, and the low bond dissociation energy in dibenzyl, indicated that the reaction

$$Ph.CH_2.CH_2.Ph \longleftrightarrow 2Ph.CH_2.$$

could be suitably investigated in this way. The attempt failed, however, as side reactions appeared to predominate.

(b) <u>The Kinetic Method</u>

Essentially, this method equates the energy of activation of the process

$$R\text{-}X \longrightarrow R. + X.$$

with the heat of dissociation of that process. This assumes that the energy of activation of the reverse process is zero.

In practice, the determination of the amounts of R. and X. produced in a specified time is very difficult, and the data available to the analyst are the amounts of products formed by secondary reactions of R. and X. with the parent compound or other substances present.

In order to apply the method, it has to be shown that the rate determining step of the total reaction is the unimolecular dissociation

$$R\text{-}X \longrightarrow R. + X.$$

or that there are reasonable grounds for assuming this to be the case. If this can be justified, the amount of the secondary product (R-Y say) is taken to indicate the amount of R. formed (or the sum of the concentrations of R-Y, R-Z, etc. if several reaction paths are available to the radical). The conditions have to be so chosen that the extent of the reverse reaction is negligible.

In applications which have been made of these general principles, interest centres mainly on the technical problems of quantitative conversion of the radicals R. produced into the substance R-Y, and on preventing reverse, and unwanted side reactions.

The earliest techniques were those of Rice (11), (12), and Paneth (13), (14), where metal mirrors

placed outside the zone of reaction were used to react with the radicals issuing from the furnace through which the reactant passed.

By using very rapid rates of flow, i.e. very short contact times, the radicals were removed from the furnace before they could react, and by extrapolation to the furnace exit of the rates of removal of standard mirrors deposited on the wall of the outlet tube, a measure of the concentration of the emerging radicals was obtained. They showed that, under the conditions of their experiments, the investigated compounds decomposed homogeneously according to a unimolecular law, and they deduced the activation energies of the primary steps.

Rice and Johnston (65) have discussed various possible objections to this technique, and have shown that even if these are valid they would have no influence on the final results. Nevertheless, the activation energies obtained are somewhat lower than what are now considered to be the best values for these dissociations, and Szwarc (4) has suggested a further inaccuracy which Rice and his collaborators did not consider, namely that the value for the rate of removal of a standard mirror at the furnace exit was deduced from measurements made at various distances

along the cold outlet tube. He considers that the behaviour of radicals in the hot zone immediately beyond the furnace would be of a different nature, and therefore the extrapolated time of removal might be in error. Forsyth (6) has also discussed this difficulty.

Thus the mirror technique, though an excellent tool for the detection of free radicals, is not the most accurate for the determination of bond dissociation energies.

(c) The Toluene Carrier Gas Technique

This method, due to Szwarc (17), employs, as a carrier gas, a compound capable of reacting rapidly with the radicals formed by the dissociation of the compound under investigation. The products of such radical captures are unreactive molecules, and stable radicals which play no further part in the reaction, but are removed by dimerisation. Within the range of its applicability, the carrier is itself unaffected by the temperatures used.

Szwarc (2), from an investigation of the pyrolysis of toluene, concluded that the dissociation proceeded through the initial rupture of the side-chain C-H bond. The highly reactive hydrogen atoms were considered to be removed by interaction with toluene

while inert benzyl radicals passed out of the furnace, and eventually dimerised.

By pyrolysing the compound under investigation in the presence of a large excess of toluene, Szwarc was able to remove the radicals formed in the dissociation by preferential reaction with the carrier. The general reaction sequence can be described as:

$R'R'' \longrightarrow R' + R''$

$Ph.CH_3 + R' \longrightarrow R'H + Ph.CH_2\cdot$

$Ph.CH_3 + R'' \longrightarrow R''H + Ph.CH_2\cdot$

$2Ph.CH_2\cdot \longrightarrow Ph.CH_2.CH_2.Ph$

The necessary conditions for the application of this method are:

1. That the dissociation energy of the weakest bond in the molecule should be considerably less than that of the side-chain C-H bond in toluene in order that no appreciable decomposition of the carrier should occur at the temperatures required for the decomposition of the reactant.
2. That the radicals formed by the dissociation should be sufficiently active to be removed immediately by reaction with toluene.

The latter condition made the toluene carrier technique unsuitable for the investigation of benzyl

iodide, as both of the radicals resulting from this are too inert to react. Bromine atoms are sufficiently active to produce HBr, and the method could therefore be successfully applied to benzyl bromide. (18)

The application of the toluene carrier technique can best be illustrated by an example from the literature.

In the pyrolysis of ethyl benzene, (17), the main decomposition products were styrene and hydrogen, with small quantities of dibenzyl and methane. Szwarc ascribed these to a chain reaction propagated by the radical $Ph.CH_2.CH_2\cdot$. He claimed that the initial dissociation formed benzyl and methyl radicals, the second of which underwent further reaction with the parent compound.

$$Ph.CH_2.CH_3 \longrightarrow Ph.CH_2\cdot + CH_3\cdot \qquad (a)$$

$$Ph.CH_2.CH_3 + CH_3\cdot \longrightarrow Ph.CH_2.CH_2\cdot + CH_4 \qquad (b)$$

$$Ph.CH_2.CH_2\cdot \longrightarrow Ph.CH{=}CH_2 + H\cdot \qquad (c)$$

$$Ph.CH_2.CH_3 + H\cdot \longrightarrow Ph.CH_2.CH_2\cdot + H_2 \qquad (d)$$

Reactions (a) and (b) were the initiators, and (c) and (d) the propagators. In the presence of excess toluene, the methyl radicals were removed by preferential reaction with the toluene, thus preventing the formation of the chain propagator.

$$Ph.CH_3 + CH_3\cdot \longrightarrow Ph.CH_2\cdot + CH_4$$

In consequence, the products were methane and dibenzyl in equimolecular proportions, and the rate of decomposition could be determined by quantitative analysis for either of these, leading to a value of 63 k.cal./mole for the dissociation energy of the $Ph.CH_2-CH_3$ bond. In the absence of a carrier, the interpretation of the data was too complex to permit any evaluation.

Szwarc and his co-workers have extended such methods to the investigation of many other compounds (19)-(22), including a series of organic bromides (e.g. (18) and (23)).

(d) Direct Determination of Radical Concentrations

As indicated above, direct measurements of the concentrations of reactive radicals in thermal decompositions are extremely difficult, and few results of value have so far been reported. Elteaton (24), using a mass spectrometer, showed that radicals could be detected during the decomposition of hydrocarbons. Lossing (25), in extending this work to many other compounds, made attempts at the estimation of radical concentrations, but admits that his quantitative data are very uncertain.

Despite such difficulties of radical estimation, the kinetic method remains the most valuable of the

existing techniques, as it has contributed the bulk of the known values of bond dissociation energies in complex molecules.

(e) Photochemical Initiation

The use of suitable carrier gases for the capture of free radicals formed during thermal decompositions offers one possible method of simplifying and studying such reactions. Another technique, which provides supplementary information of great relevance, is the use of radiant energy to produce the primary dissociation of the substance under investigation. This enables a primary dissociation to be conducted at a controlled rate which is reasonably independent of temperature, and so permits the effect of this variable on the secondary processes to be isolated for study. It is necessary, of course, that the secondary processes shall not be affected by the frequencies of light used.

A classical example, and one which has been discussed fully by many authors (26), is the study, by Bodenstein and his co-workers (27), (28), of the reaction between hydrogen and bromine.

A recent application of similar techniques, and theories, and one which is of direct interest from

the point of view of this thesis, is the study by van Artsdalen (29) - (33) of the photobromination of hydrocarbons. Essentially it entails the determination of the activation energies of the reactions RH + Br. ⟶ R. + HBr and R. + HBr ⟶ RH + Br. and the combination of these to give the heat of the reaction. This can then be used in conjunction with the heat of reaction for HBr ⟶ H. + Br. to give $\triangle H$ for RH ⟶ R. + H. and hence, assuming zero activation energy for the reverse process, the bond dissociation energy D(R-H).

The earliest work in this field was the investigation of the photobromination of methane by Mlotinkowsky and van Artsdalen (29). Employing a photometric technique for the determination of the rate of removal of bromine, they showed that the rate of bromination was proportional to $(CH_4)(Br_2)^{1/2} \times (1/P)^{1/2}$ where P is the total pressure in the system. Hydrogen bromide was found to inhibit the reaction and bromination in excess HBr was shown to conform to the rate equation

$$\frac{-d.}{dt}(Br_2) = \frac{k'.(CH_4)(Br_2)^{1/2}(1/P)^{1/2}}{1 + \frac{k_4(HBr)}{k_3(Br_2)}}$$

This could be explained by the mechanism

$Br_2 + h\nu \longrightarrow Br\cdot + Br\cdot$ 1.

$Br\cdot + CH_4 \longrightarrow CH_3\cdot + HBr$ 2.

$CH_3\cdot + Br_2 \longrightarrow CH_3Br + Br\cdot$ 3.

$CH_3\cdot + HBr \longrightarrow CH_4 + Br\cdot$ 4.

$Br\cdot + Br\cdot + M \longrightarrow Br_2 + M$ 5.

The overall activation energy of the uninhibited reaction was studied over a temperature range of 50°C, and the value of 17.8 k.cal./mole ascribed to reaction 2., as was reasonable from the nature of the rate equation. The temperature coefficient of the inhibited reaction gave values of k_4/k_3 from which resulted a value of 2 k.cal./mole for $E_4 - E_3$. Assumption of zero activation energy for the exothermic radical reaction 3. gave E_4 = 2 k.cal./mole.

Thus, by equating E_2 for the forward, and E_4 for the reverse reactions,

$$CH_4 + Br_2 \underset{k_4}{\overset{k_2}{\rightleftharpoons}} CH_3\cdot + HBr$$

the heat of reaction, $\triangle H$ = 15.8 k.cal./mole was obtained.

The heat of reaction for the participants in their standard states was calculated as $\triangle H_o^\circ$ = 15.6 k.cal./mole.

Thus,

$CH_4 + Br. \longrightarrow CH_3. + HBr$ $\quad \triangle H = 15.0$ k.cal.

$HBr \longrightarrow H. + Br.$ $\quad \triangle H = 85.8$ k.cal.

$CH_4 \longrightarrow CH_3. + H.$ $\quad \triangle H = 100.8$ k.cal.

Assuming zero activation energy for the reverse process, they thus obtained the bond dissociation energy $D(CH_3\text{-}H) = 101$ k.cal./mole at $0^\circ K$, a value which is in excellent agreement with those achieved by other methods.

Other compounds investigated by van Artsdalen (30)-(35) have given results which correspond closely to the accepted values, with the exception of that for toluene (32) for which the bond dissociation energy of $D(Ph.CH_2\text{-}H) = 89.9$k.cal./mole differs greatly from that obtained by pyrolysis (2). A detailed account of the possible reasons for the discrepancy will be given later in this section (page 34.).

Electron Impact

Hitherto, the methods described have employed radiant energy to produce the necessary dissociation of the molecule. It is also possible to use for this purpose the kinetic energy of fast moving electrons (43)(44).

When a stream of molecules is subjected to electron

bombardment in a mass spectrometer, the molecule ion, and the ions of many fragments, can be detected at the collector plate of the instrument. (See for example Table 4, page 71). The reactions can be represented as e.g.

$$R.CH_3 + e \longrightarrow R.CH_3^{\bullet} + 2e$$

$$R.CH_3 + e \longrightarrow R.CH_2^{\bullet}. + H. + 2e$$

$$R.CH_3 + e \longrightarrow R^{\bullet}. + CH_3. + 2e$$

Obviously, if the ion $R.CH_2^{\bullet}.$ is present in the mass spectrum, the electrons causing this dissociation must possess kinetic energy at least as great as the sum of the bond dissociation energy $D(R.CH_2\text{-}H)$ and the ionisation potential of the radical $I^z(R.CH_2^{\bullet}.)$.

Thus, if R.H molecules are fed into the ionisation chamber, the minimum potential necessary to produce $R^{\bullet}$ ions, i.e. the appearance potential, should equal the above sum.

$$R.H \longrightarrow R^{\bullet} + H. + e$$

$$A_1(R^{\bullet}) = I^z(R^{\bullet}) + D(R\text{-}H)$$

The ionisation potentials of some radicals are known spectroscopically (e.g.(66), (79)), but if such data are not available, the required value can be determined by electron impact, by feeding free radicals R., produced generally by pyrolysis, into the ionisation chamber, and once more determining the appearance

potential of the ion $R^{\cdot}$

$$R^{\cdot} \longrightarrow R^{\cdot +} + e - A_2(R^{\cdot})$$

$$A_2(R^{\cdot}) = I^{\Sigma}(R^{\cdot +})$$

Hence, by subtraction,

$$D(R\text{-}H) = A_1(R^{\cdot}) - A_2(R^{\cdot})$$

The determination of appearance potentials is not, however, a simple process. The potential applied across the electron accelerating plates is not necessarily the potential operative in the acceleration of the electrons, as films of hydrocarbons, deposited on the plates, can set up contact potentials reducing the effective acceleration considerably. Further, the electron beam is not truly monochromatic, some electrons having initial kinetic energy, and so their energy on entering the chamber may be greater than the value calculated from the applied potential.

The first of these two sources of error may be eliminated to some extent by streaming into the chamber a mixture of R.H and some gas, generally one of the inert gases, for which the appearance potential of an ion is known accurately - e.g. $Ne \longrightarrow Ne^{+} + e$. The observed appearance potentials for Ne^{+} and $R^{\cdot}$ are measured concurrently, and a measure of the "sensitivity" of the instrument obtained. In this way, a correction can be applied, giving a closer approximation to the true

potential.

Another source of serious error lies in the possibility that some of the dissociation fragments may be formed in an electronically excited state, in which case the observed appearance potential will contain an excitation energy term and will yield a value for the bond dissociation energy which is too large by this amount. For example, Douglas and Herzberg (42), by a spectroscopic method, showed that the mass spectrometrically determined value for the ionisation potential $I^{E}(CH_{\bullet}^{+})$, obtained from HCN, included 99.5 k.cal./mole excess energy. Thus, errors of considerable magnitude can result from electron impact data. The radicals produced from polyatomic molecules may possess considerable vibrational energy, and this also may introduce errors which can attain serious proportions. Hence the electron impact data must be regarded as supplying an upper limit to the bond dissociation energy, rather than an exact value.

A second approach with this technique involves measurements of the appearance potentials for the $R_{\bullet}^{+}$ ion from two different sources R.X where X is generally H. and R.

i.e. $R.H \longrightarrow R_{\bullet}^{+} + H_{\bullet} + e \qquad -A_1(R_{\bullet}^{+}) \qquad (1).$

$R.R \longrightarrow R_{\bullet}^{+} + R_{\bullet} + e \qquad -A_2(R_{\bullet}^{+}) \qquad (2).$

Subtracting (1) from (2).

$$\triangle H_f(R.R) - \triangle H_f(R.H) = \triangle H_f(R.) - \triangle H_f(H.) + A_1(R^{\bullet}) - A_2(R^{\bullet})$$

But $D(R-H) = \triangle H_f(R.) + \triangle H_f(H.) - \triangle H_f(R.H)$

$\therefore D(R-H) = \triangle H_f(R.R) - 2\triangle H_f(R.H) + 2\triangle H_f(H.) - A_1(R^{\bullet}) + A_2(R^{\bullet})$

Thus from the difference in the appearance potentials, together with knowledge of the heats of formation of the starting materials and of hydrogen atoms, the bond energy D(R-H) can be calculated.

The advantages of this approach are that ionisation data for the radical $R^{\bullet}$ are not required, and many instrument variations are eliminated, provided both measurements are made on the same instrument within a short period.

That this method is reliable is shown by the agreement obtained by Stevenson (43) with the accepted values for many dissociations.

$D(CH_3-H) = 101 \pm 4.5$ k.cal./mole.

$D(C_2H_5-H) = 96.7 \pm 4.5$ k.cal./mole.

$D(CH_3-CH_3) = 82.5 \pm 9$ k.cal./mole.

$D(C_2H_5-C_2H_5) = 77.6 \pm 9$ k.cal./mole.

As the accuracy of this work is seldom better than $\pm$ 5 k.cal./mole., the chief advantage of the method is its ability to differentiate between conflicting values

obtained in other ways.

Some Applications of the General Methods to the Dibenzyl Problem

The problem of determining the strength of the central C-C bond in dibenzyl is also the problem of determining the heat of formation of the benzyl radical. Thus the heat of dissociation is given by the ΔH value for the reaction

$$Ph.CH_2.CH_2.Ph_{(g)} \longrightarrow 2Ph.CH_2.(g)$$

The heat of formation of dibenzyl being well known, it is obvious that any conclusions regarding the heat of formation of the benzyl radical would solve the bond energy problem.

Values for this quantity have been obtained by a variety of methods applied to compounds of the type $Ph.CH_2.X$, in association with knowledge of the thermal constants of these compounds and of X. It is the purpose of the succeeding pages to survey the evidence obtained.

The available data can be divided into five groups.

(1) The work of Szwarc on the pyrolysis of toluene.

(2) The re-examination by Steacie of the pyrolysis of toluene.

(3) The pyrolysis of related compounds.

(4) The photobromination of toluene by van Artsdalen.

(5) Electron impact studies on toluene and dibenzyl.

The Szwarc Data on Toluene

Applying a kinetic flow technique, Szwarc investigated the pyrolysis of toluene in the temperature range 680°C-850°C at partial pressures of 2mm - 15 mm. The conditions were chosen to enable a range of decompositions from 0.01% - 1.0% to be investigated conveniently. Although trouble was taken to ensure the purity of the starting material, it was found that sufficient impurity remained to cause considerable side reactions, so the experiments were performed with toluene which had previously undergone pyrolysis to remove this.

Investigation of the resultants showed hydrogen, methane, and dibenzyl as the main products. Hydrogen and methane were estimated by combustion analysis, and found to be in the ratio 60:40. Dibenzyl was characterised by melting point and mixed melting point determinations and its concentration estimated. It corresponded roughly to the sum of the gases, i.e. 1 mole of dibenzyl was produced for every mole of $H_2 + CH_4$. No ethane could be observed.

From variations in pressure, contact time, and surface, it was inferred that the reaction was homogeneous

and first order. The mechanism proposed was a rate determining rupture of the side chain C-H bond,

$$Ph.CH_3 \longrightarrow Ph.CH_2\cdot + H\cdot \qquad 1.$$

followed by a sequence of fast reactions

$$Ph.CH_3 + H\cdot \longrightarrow Ph.CH_2\cdot + H_2 \qquad 2.$$

and
$$Ph.CH_3 + H\cdot \longrightarrow Ph.H + CH_3\cdot \qquad 3a.$$
$$Ph.CH_3 + CH_3\cdot \longrightarrow Ph.CH_2\cdot + CH_4 \qquad 3b.$$

or
$$Ph.CH_3 + H\cdot \longrightarrow Ph\cdot + CH_4 \qquad 4a.$$
$$Ph.CH_3 + Ph\cdot \longrightarrow Ph.CH_2\cdot + Ph.H \qquad 4b.$$

the benzyl radicals being removed by dimerisation.

$$2Ph.CH_2\cdot \longrightarrow Ph.CH_2.CH_2.Ph \qquad 5.$$

Rate determinations made from measurements of the rate of production of total gases ($CH_4 + H_2$), assuming the above mechanism, gave the rate equation

$$k(sec^{-1}) = 2.10^{13}\exp.(-77,000/RT)$$

The mechanism accounted for the observed products, and postulated the presence of benzene as a resultant, though no attempt was made to identify it.

Of the two possible paths, 3. and 4., suggested for the production of methane, Szwarc considered the former more likely on energetic grounds. The validity of the dissociation energy of 77.5 k.cal./mole depended on the acceptance of reactions 3a. and 3b. as secondary processes. The constancy of the methane/hydrogen ratio regardless of conditions would appear to justify this

assumption, but it is obvious that the bond energy value would be less certain if methane was formed by the reaction

$$Ph.CH_3 \longrightarrow Ph. + CH_3.$$

occurring simultaneously with reaction 1.

The Re-examination by Steacie (34)

The apparatus and procedures employed by Steacie were essentially similar to those of Szwarc, differing significantly only in the range of contact times and the very high temperatures investigated. The results, however, showed little agreement with the previous work.

The production of hydrogen and methane was confirmed, but in the ratio 69/31, as compared with the Szwarc value of 60/40. This figure was essentially independent of conditions. Benzene, postulated by Szwarc, was identified, and its concentration shown to correspond roughly to that of methane. A small quantity of styrene was also found.

Ultra-violet spectrophotometric analysis of the non-volatile products revealed the characteristic absorption of the diphenyl nucleus, and, by chromatographic separation, this was ascribed to a mixture of the isomers of dimethyl diphenyl. Dibenzyl was also found, and was shown to be as little as 50% of the non-volatile materials.

The most significant deviation, however, was the claim by Steacie of non-first-order behaviour. Investigations of the variation of contact time exhibited a two-fold variation in the rate of (H_2 + CH_4) formation over the range 0.068 sec.-0.568 sec. Variations of pressure and surface area also affected the rate, though to a lesser degree.

For a series of experiments at a contact time of 0.068 sec., the logarithm of the first order velocity constant was plotted against $1/T^{\circ}K$, and an activation energy of 90 k.cal./mole obtained. Thus, even if first order behaviour was assumed, the value for $D(Ph.CH_2-H)$ was widely different from that quoted by Szwarc.

In an attempt to explain the formation of dimethyl diphenyls by further reactions of dibenzyl, small concentrations of dibenzyl were pyrolysed in the presence of toluene under conditions similar to those used for toluene alone. At the temperatures used, toluene is decomposed to the extent of 0.73%, so this contribution to the products was deducted from the resultants.

The most important observation of these experiments was the absence of methane from the gaseous products. More hydrogen was formed than could be accounted for by the decomposition of toluene and the formation of stil-

bene and anthracene. Loss of dibenzyl was also noted, this being as much as 39% of the quantity injected.

On this evidence Steacie has stated:- "No methane was formed in the presence of toluene, although considerable hydrogen was produced. In view of the fact that there was more hydrogen than stilbene, it seems likely that hydrogen atoms were in existence at some time in the reaction. This would seem to cast some doubt on the feasibility of the reaction H. + $Ph.CH_3 \longrightarrow Ph.H + CH_3.$" However, the alternative suggestion which he puts forward for the formation of methane, that the reaction

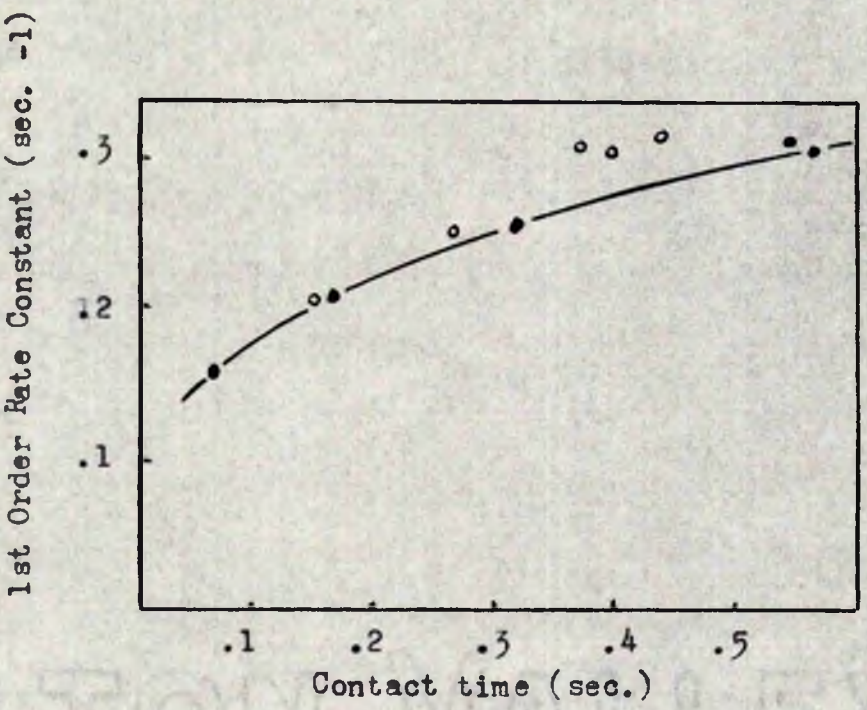
$$Ph.CH_3 \longrightarrow Ph. + CH_3.$$

takes place concurrently, would also seem to be disproved, as the presence of dibenzyl should not affect this process at all.

Discussion

The variation of the first order rate constant with contact time, as observed by Steacie, would appear to make both values for the bond energy of toluene invalid. However, as stated earlier, the contact times used by the two workers differed appreciably. Szwarc investigated the effect of reaction time variations over the range 0.235 - 0.905 sec. whereas Steacie used times as low as 0.068 sec. Moreover, in

Figure 1.



• Pressure about 1.2 cm. Hg.

° Pressure about 2.0 cm. Hg.

the latter case, the reaction vessel used in determining the rate variations was only 24 cm. long. It is doubtful if the data obtained at such short intervals gives a true account of the reaction, as it is possible that the reactant was not in the furnace long enough to attain the temperature of the surroundings. This would result in low decompositions and hence abnormal rate constants. It can be seen from Fig.1 that the plot of rate constant against contact time approaches a horizontal line in the region investigated by Szwarc. Moreover, variations of the toluene pressure had no marked effect, and the rate constants, plotted on the same graph, correspond fairly well.

The difference of 12.5 k.cal./mole between the two values of the toluene bond energy is not surprising if the above suggestion is correct, as the data from which the 90 k.cal. value is calculated were obtained using a contact time of 0.068 sec., i.e. in the region in which the rate values are doubtful. The temperature range of this investigation was very much higher than that used by Szwarc, there being an overlap of a few degrees only. Thus the nature of the reaction under the two sets of conditions may vary considerably, so comparison of the results may not be justified. It is strange that since

the stated intention of Steacie was to repeat Szwarc's work, the conditions he selected did not correspond to those used previously.

On the other hand, the work of Szwarc did not include an exhaustive investigation of the secondary processes, and it may be that his reaction mechanism is incomplete. The majority of Steacie's re-investigation has been concerned with the study of reaction products, and he has identified many compounds undetected by Szwarc. However, the value of 77.5 k.cal./mole cannot be invalidated unless it can be shown that the mechanisms postulated for the formation of hydrogen and methane are inaccurate or incomplete, and this Steacie has been unable to do. He has suggested that the formation of methane occurs by a reaction which takes place concurrently with the dissociation

$$Ph.CH_3 \longrightarrow Ph.CH_2\cdot + H\cdot$$

but the evidence obtained from his experiments with dibenzyl would seem to disprove this. The occurrence of dimethyl diphenyls, stilbene, and styrene could not affect the primary processes, and hence have no influence on the bond energy.

Supporting Evidence from Compounds of the Type $Ph.CH_2.X$

It is obvious that since the heats of formation of toluene and hydrogen atoms are known, it is possible to determine the heat of formation of the benzyl radical from any determined value for the strength of the side chain C-H in toluene.

Thus

$$\Delta H_{f(g)}(Ph.CH_3) = \Delta H_{f(g)}(Ph.CH_2\cdot) + \Delta H_{f(g)}(H.) - D(Ph.CH_2-H)$$

$\Delta H_{f(g)}(Ph.CH_3)$ = 11.9 k.cal./mole. (35)

$\Delta H_{f(g)}(H.)$ = 52.0 k.cal./mole. (36)

$D(Ph.CH_2-H)$ = 77.5 k.cal./mole. (2)

$\therefore$ $\Delta H_{f(g)}(Ph.CH_2\cdot)$ = 37.4 k.cal./mole.

if we accept temporarily the dissociation energy found by Szwarc. Using this value of 37.4 k.cal./mole, we can calculate the heats of formation of other radicals X. if the dissociation energies $D(Ph.CH_2-X)$ are known. i.e. $\Delta H_f(Ph.CH_2X) = \Delta H_f(Ph.CH_2\cdot) + \Delta H_f(X.) - D(Ph.CH_2-X)$ Th values of $\Delta H_f(X.)$ obtained in this way can be compared with those from other methods, and the validity of the heat of formation of the benzyl radical checked.

Such an approach has been used by Szwarc to justify his work on toluene. The values of $D(Ph.CH_2-X)$ have been obtained for a series of radicals X. by means of the toluene carrier gas technique. The results are

Table 1

X.	ΔH_f(Bz.X)	D(Bz-X)	ΔH_f(X.)	ΔH_f(X.) from other sources
CH_3. (17)	7.1	63.	32.7	32.1
C_2H_5.(38)	1.9	57.5 ± 4	22 ± 4	25.3
Br. (18)	15.6 ± 3	50.5 ± 2	28.7 ± 4	22.7
NH_2. (20)	15.0 ± 3	59 ± 4	46.6 ± 4	41.0 ± 2

summarised in Table 1. The heats of formation of the compounds $Ph.CH_2.X$ are taken from the data collected by Roberts and Skinner, (35), as are the values of $\triangle H_f(X.)$ for $X. = CH_3.$ and $C_2H_5.$ in the last column. The heat of formation of bromine atoms is from spectroscopic data, and $\triangle H_f(NH_2.)$ from toluene carrier experiments on hydrazine (19).

$\triangle H_f(Ph.CH_2.) = 37.4$ k.cal./mole was used to calculate the $\triangle H_f(X.)$ values in column 4.

In the case of ethyl benzene, the correspondence between the two values for the heat of formation of the methyl radical is very good. For the others, experimental difficulties have caused some degree of uncertainty in the bond energy values, and this, coupled with doubtful values for the heats of formation of benzyl bromide and benzylamine, has resulted in considerable uncertainty as to the correct figures to be assigned to the heats of formation of the respective radicals. The correspondence in these three cases is poor, but with the exception of the benzyl bromide value, the difference lies within the experimental accuracy.

No such agreement could be obtained if the heat of formation of the benzyl radical was calculated from Steacie's results.

<u>The Photobromination of Toluene</u>

Anderson, Scheraga, and van Artsdalen (3) have studied the kinetics of the bromination of toluene both thermally and photochemically by the technique discussed earlier. The reaction conditions were:

Toluene pressure 67.1 - 192.8 mm.

Bromine pressure 9.15 - 32.30 mm.

Temperature range 80°C - 135°C for the photochemical experiments,

166°C for the thermal experiments.

The photochemical reaction was activated by light of wavelength 4890Å, in which region bromine is the only substance in the reaction mixture which absorbs, dissociating to give one excited, and one normal atom. The rate of reaction was determined by measuring photometrically the rate of loss of bromine from the system.

A few thermal runs were performed to illustrate that the observed reaction rates could be accounted for by a mechanism similar to that ascribed to the photodecomposition.

The nature of the reaction products was investigated by infra-red spectroscopy, the absorption data indicating the presence of benzyl bromide, and showing no characteristic absorption bands of the bromotoluenes. The initial reaction rates were determined from the initial slope of the rate / time curves, and shown to

satisfy the expression

$$\frac{-d(Br_2)}{dt} = k.(Br_2)^{\frac{1}{2}}(R.H) \qquad (a)$$

From experiments performed in the presence of excess HBr, the rate of the inhibited reaction was investigated, and the inhibition constants calculated by applying the equation

$$\frac{-d(Br_2)}{dt} = \frac{k.(Br_2)^{\frac{1}{2}}(R.H)}{1 + \frac{a(HBr)}{(Br_2)}} \qquad (b)$$

From this evidence the following mechanism was ascribed to the reaction.

$Br_2 + h\nu \longrightarrow 2Br.$ 1.

$Br. + R.H \longrightarrow R. + HBr$ 2.

$R. + Br_2 \longrightarrow R.Br + Br.$ 3.

$R. + HBr \longrightarrow R.H + Br.$ 4.

$Br. + Br. + M \longrightarrow Br_2 + M$ 5.

The temperature dependence of the rate constants derived from equation (a) for the uninhibited, and from (b) for the inhibited reactions gave activation energies for the reactions 2. and 4. These were

$E_2 = 7.2$ k.cal./mole.

$E_4 = 5.0$ k.cal./mole.

Hence the heat of reaction $\triangle H$ for

$R.H + Br. = R. + HBr$

is given by $\triangle H = E_2 - E_4 = 7.2 - 5.0 = 2.2$ k.cal./mole. The C-H bond energy in toluene can then be calculated.

$$R.H + Br. \longrightarrow R. + HBr \qquad \triangle H = 2.2 \text{ k.cal./mole.}$$

$$HBr \longrightarrow H. + Br. \qquad \triangle H = 87.7 \text{ k.cal./mole.}$$

$$\therefore \quad R.H \longrightarrow R. + H. \qquad \triangle H = 89.9 \text{ k.cal./mole.}$$

This in turn yields a value of 48.4 k.cal./mole. for the heat of formation of the benzyl radical.

The estimated error in the determination was $\pm$ 1.3 k.cal./mole.

Discussion

The toluene bond energy obtained by this method is in very close agreement with that which Steacie found, but since he states that the pyrolysis of toluene is not first-order, this agreement cannot have great significance. Nevertheless, the photobromination technique, applied to aliphatic hydrocarbons, has produced much satisfactory data, and the results for toluene cannot therefore be disregarded.

It is unfortunate that an attempt was not made to estimate quantitatively either of the products, viz. benzyl bromide and HBr. Nor was there any detailed qualitative investigation, what analyses there were consisting mainly of attempts to distinguish between benzyl bromide and bromotoluene.

The accuracy of the experiments depended on the assumption that only the postulated reactions occurred, and that no other possibilities existed for the removal

of bromine from the system. Since it has been shown that benzyl radicals are much less reactive than alkyl radicals, it is conceivable that reactions 3. and 4. do not remove all the radicals formed, and that other mechanisms are available for their disposal. The present investigation has shown that dimerisation of this species is rapid, and that the tendency to take part in side reactions is very small. Thus it may be that dibenzyl forms one of the products, and as one would expect the C-H bond energy of this to be somewhat less than 77.5 k.cal./mole, it is possible that bromination of dibenzyl occurs simultaneously. Whether or not this does in fact happen could be decided if dibenzyl or stilbene appeared in the product mixture, but this possibility does not appear to have been investigated by van Artsdalen and his colleagues.

Loss of bromine by some undetected mechanism would not affect the activation energy if the ratio of unknown to total reaction remained constant over a range of temperature. This would be true if the unknown reaction was of a secondary nature. If, however, it is postulated that bromination of dibenzyl does take place concurrently, the difference in bond energy between dibenzyl and toluene would result in variations in the ratio of the respective reaction

rates which could seriously affect the accuracy of any conclusions drawn from the experiments.

Further Evidence

Recently, new data appertaining to the subject has been forthcoming in the form of electron impact studies. Schissler and Stevenson (39) have examined the mass spectra of toluene and dibenzyl, and measured the appearance potentials of the benzyl radical in each case.

Assuming that the appearance potentials of the $C_7H_7^+$ ion in the mass spectra of toluene and dibenzyl have the significance,

$$Ph.CH_3 = C_7H_7^+\cdot + H\cdot + e\cdot$$

$$A_1(C_7H_7^+) = D(Ph.CH_2\text{-}H) + I^R(Ph.CH_2\cdot) \qquad (1)$$

$$Ph.CH_2.CH_2.Ph = C_7H_7^+\cdot + Ph.CH_2\cdot + e\cdot$$

$$A_2(C_7H_7^+\cdot) = D(Ph.CH_2\text{-}CH_2.Ph) + I^R(Ph.CH_2\cdot) \qquad (2)$$

the appearance potentials observed were

$$A_1(C_7H_7^+\cdot) = 11.58 \pm 0.1 \text{ ev/molecule.}$$

$$A_2(C_7H_7^+\cdot) = 10.53 \pm 0.1 \text{ ev/molecule.}$$

Subtracting equation (1) from equation (2) we get,

$$(Ph.CH_2\cdot)_2 + H\cdot = Ph.CH_3 + Ph.CH_2\cdot$$

$$\triangle H = A_2(C_7H_7^+\cdot) - A_1(C_7H_7^+\cdot)$$

$$= -1.32 \text{ ev/molecule.} \qquad (3)$$

From the heats of formation of toluene (36), dibenzyl (35), and hydrogen (35), we can then compute,

$$(Ph.CH_2\cdot)_2 + 2H\cdot = 2Ph.CH_3$$

$$\triangle H = -4.66 \text{ ev/molecule.} \qquad (4)$$

Subtracting (4) from (3) we get,

$$Ph.CH_2\text{-}H = Ph.CH_2\cdot + H\cdot$$

$$D(Ph.CH_2\text{-}H) = 4.66 - 1.32 = 3.44 \text{ ev/molecule.}$$

$$= 77.0 \pm 3.0 \text{ k. cal./mole.}$$

The benzyl radical appearance potential in ethyl benzene has also been determined, and from knowledge of the heats of formation of toluene, ethylbenzene (35) and the methyl radical (40), $A(C_7H_7^+\cdot)$ has been calculated for toluene. The value so obtained was 11.85 ± 0.1 ev/molecule, in excellent agreement with the value obtained directly, giving some indication of the self-consistency of the data.

An attempt to evaluate the ionisation potential $I^B(C_7H_7\cdot)$ has been made by Lossing, Ingold and Henderson (41). Their value of 7.75 ± 0.08 ev/molecule can be combined with Stevenson's appearance potential in equation (1) above to yield the C-H bond dissociation energy directly. The result obtained is 95 ± 5 k.cal./mole. At first sight, this would appear to support the photobromination data, but the reliability of ionisation potential values is questionable, and it is doubtful if it is justifiable to include this material in the present discussion.

Summary

All the above investigations point to two conflicting values for D(Ph.CH_2-H) :- 77.5 k.cal./mole, and 89.9 k.cal./mole. Support for the latter figure is weak, as Steacie does not consider himself justified in ascribing a value calculated from first-order constants to a dissociation which does not appear to obey a first-order law, and ionisation potential data are not sufficiently reliable to give more than an upper limit to the bond energy. Moreover, several possible sources of error have been suggested, and until these have been disproved, this value must remain suspect. It is, however, only a few months from the time of writing since this new figure was published, and it may be that further evidence will be forthcoming shortly.

The more established value of 77.5 k.cal./mole has in its support the excellent agreement obtaining when applied to the determination of other bond dissociation energies. It is difficult, therefore, to doubt a value which can be corroborated in so many ways. Stevenson's electron impact data are also self consistent, and agree admirably with Szwarc.

As stated, the main weakness in Szwarc's work is the possibility that his interpretation of the reaction

mechanism may be in error. Steacie has shown the presence of species undetected by his predecessor, but the temperatures at which these were found were above the range investigated by Szwarc, and possibly they do not occur in the lower temperature region. Evidence has been produced both for and against the reaction

$$Ph.CH_3 + H. \longrightarrow Ph.H + CH_3.$$

but neither claim is conclusive.

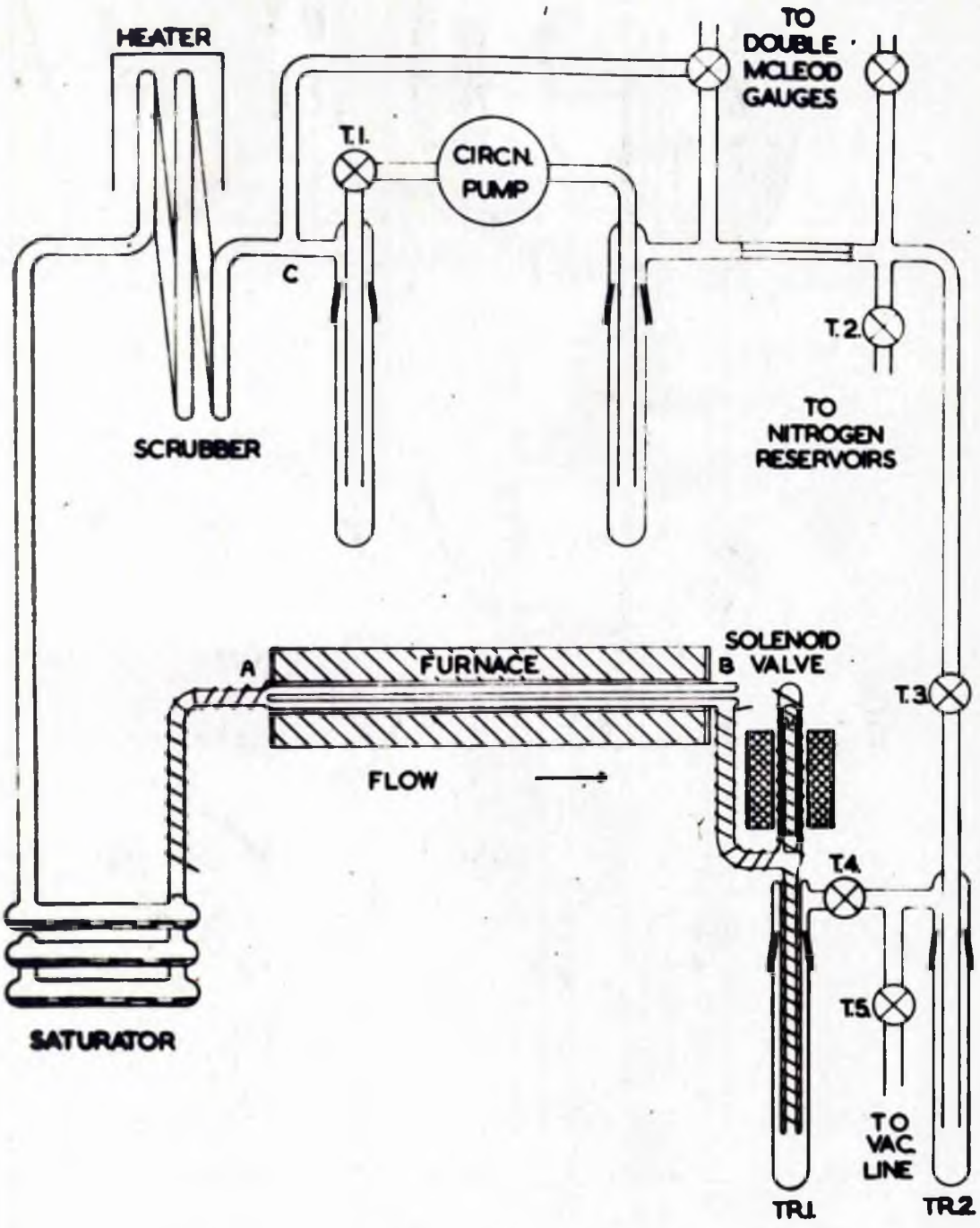
One must conclude therefore that although there is doubt as to the value to be ascribed to the reaction

$$Ph.CH_3 \longrightarrow Ph.CH_2. + H.$$

the weight of evidence is in favour of the earlier value of 77.5 k.cal./mole.

Figure 2

Pyrolysis Apparatus



THE PRESENT INVESTIGATION

The object of the present investigation was to examine the anomalous temperature independent factor obtained by Miles. It was intended first to perform a few preliminary experiments to corroborate his values, using more satisfactory analytical techniques. If his value proved to be correct, further investigations into the reasons for the anomaly would be carried out.

The Apparatus

Essentially, the apparatus constructed for the preliminary work was identical with that employed by Miles, modifications being introduced only for the pick-up of reactant and collection of products.

In outline it consisted of a closed system in which nitrogen at a pressure of 4-5mm.Hg. was circulated by means of a pump. The gas, passing through a "saturator", carried the vapour of the reactant through the reaction vessel which was maintained at a suitable temperature. On emerging from the high temperature zone, it then passed through a series of cold traps in which the unchanged dibenzyl and the reaction products condensed, the nitrogen returning to the pump for recycling. A simplified diagram is shown in Figure 2. The other necessities were a

device for measuring the rate of flow of the gases, and a thermocouple to determine the temperature of the reaction vessel.

The Saturator

For the early work this consisted of a series of three trays, each carrying several grams of dibenzyl, immersed in a thermostatically controlled oil bath, the temperature of which was adjusted to give a suitable vapour pressure of reactant. The circulating nitrogen stream, passing over the hot dibenzyl, picked up the vapour and carried it through the reaction vessel. To ensure approximate saturation of the nitrogen stream, three trays were considered necessary.

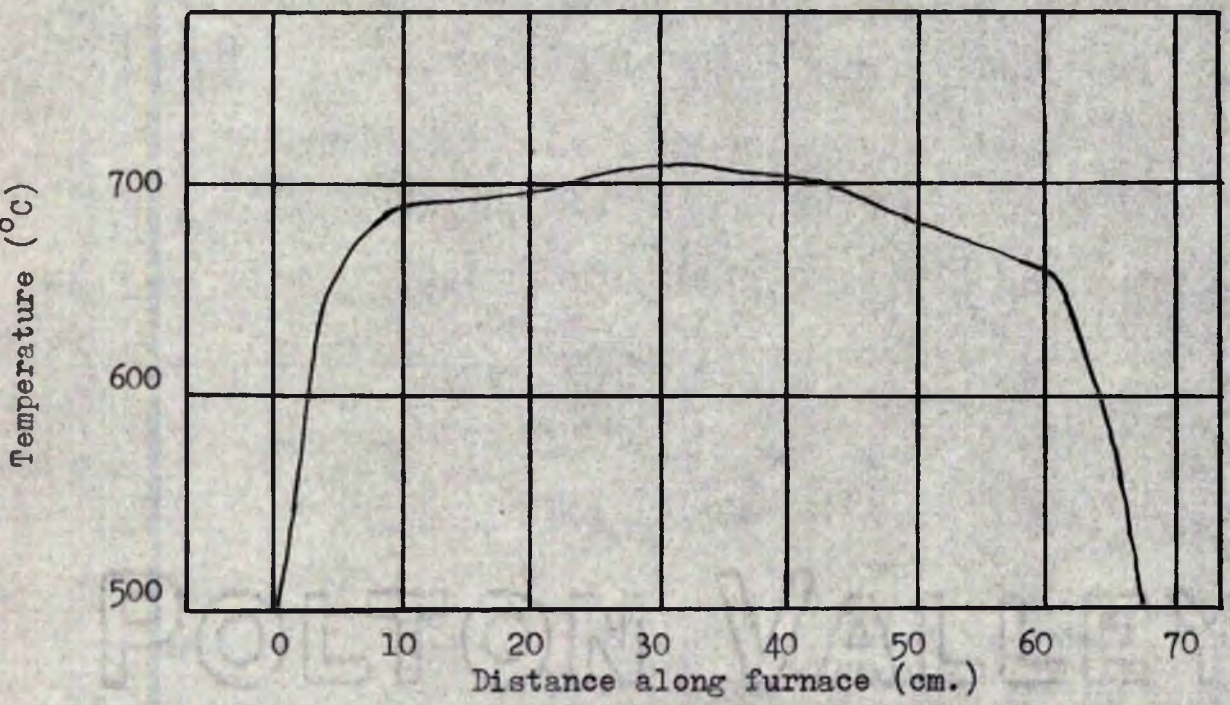
The Reaction Vessel

This was constructed from two concentric silica tubes, the outer being 70cm. long, 18 mm. internal diameter, the inner, 65cm. long and 8mm. outside diameter, the smaller was sealed at one end, and served as a pocket for the hot junction of the Chromel/Alumel thermocouple which was used to determine the temperature of the vessel. The silica vessel was attached to the inlet and outlet Pyrex leads of the circulating system by standard conical ground glass joints sealed with "Polythene" wax. Before use, the whole vessel was thoroughly cleaned with hydrofluoric acid.

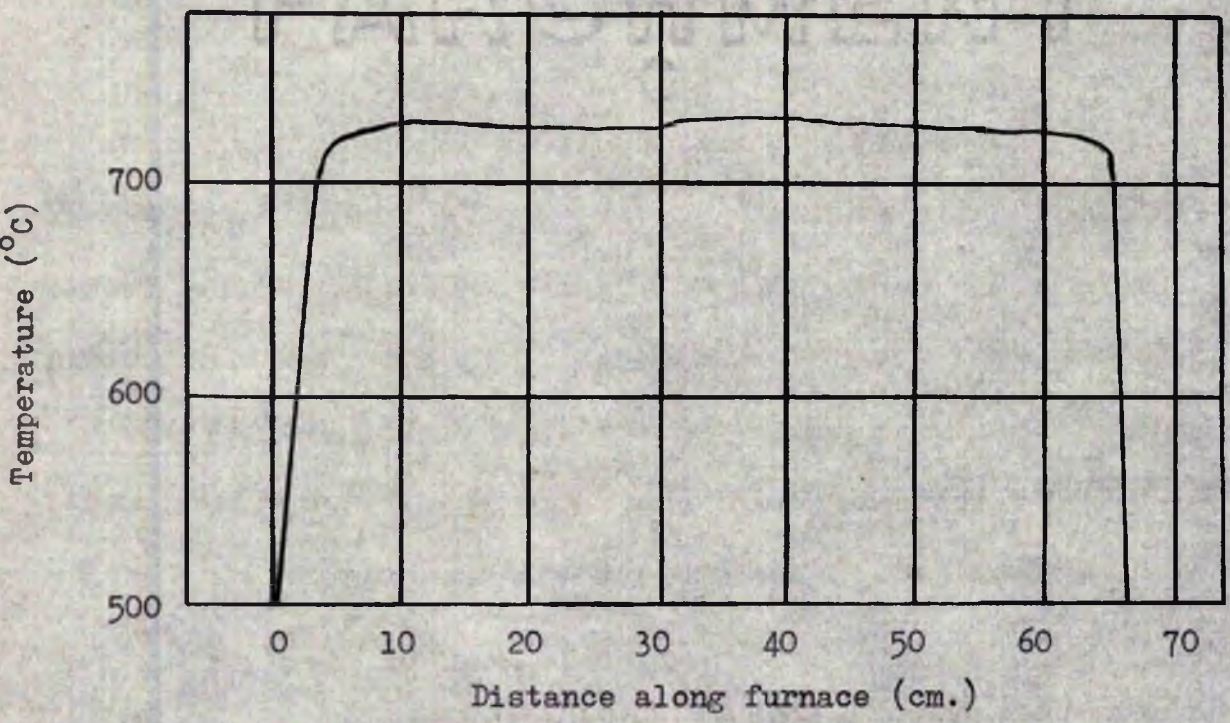
Figure 3

Furnace Temperature Distribution

(a) Before Smoothing



(b) After Smoothing



The Furnace

The foundation for the electric furnace was a tube of "Inconel" alloy, 60cm. long, 5cm. diameter, covered with a 1/4" layer of alundum cement. On this was wound the heating element of "Nichrome" tape, one turn/cm. in the middle, two turns/cm. over the last 5cm. at each end, the windings being tapped at 10cm. intervals. The whole was covered with a further layer of cement and encased in a section of magnesia pipe lagging.

The heater windings were connected in series with an ammeter to the secondary of a Variac transformer which was coupled to the mains through a constant voltage transformer to free the furnace from variations in mains voltage. Approximately 3 amps were required to give a temperature of 600°C.

In this state, the temperature at different points along the central axis of the furnace varied widely. "Smoothing" was performed by placing shunts across the centre tappings and adjusting these until the temperature along the whole length of the furnace was constant to ± 2°C. Plots of temperature against distance from one end of the furnace before and after smoothing are shown in Figure 3. The uniform portion between the lines A and B was taken to be the effective furnace length, and

the effective volume of the reaction vessel, that volume which lay between these two positions. The latter was measured with a burette, and was found to be 139 ml. The uniformity was checked at intervals during the subsequent investigations as the temperature distribution was found to vary with ageing of the furnace.

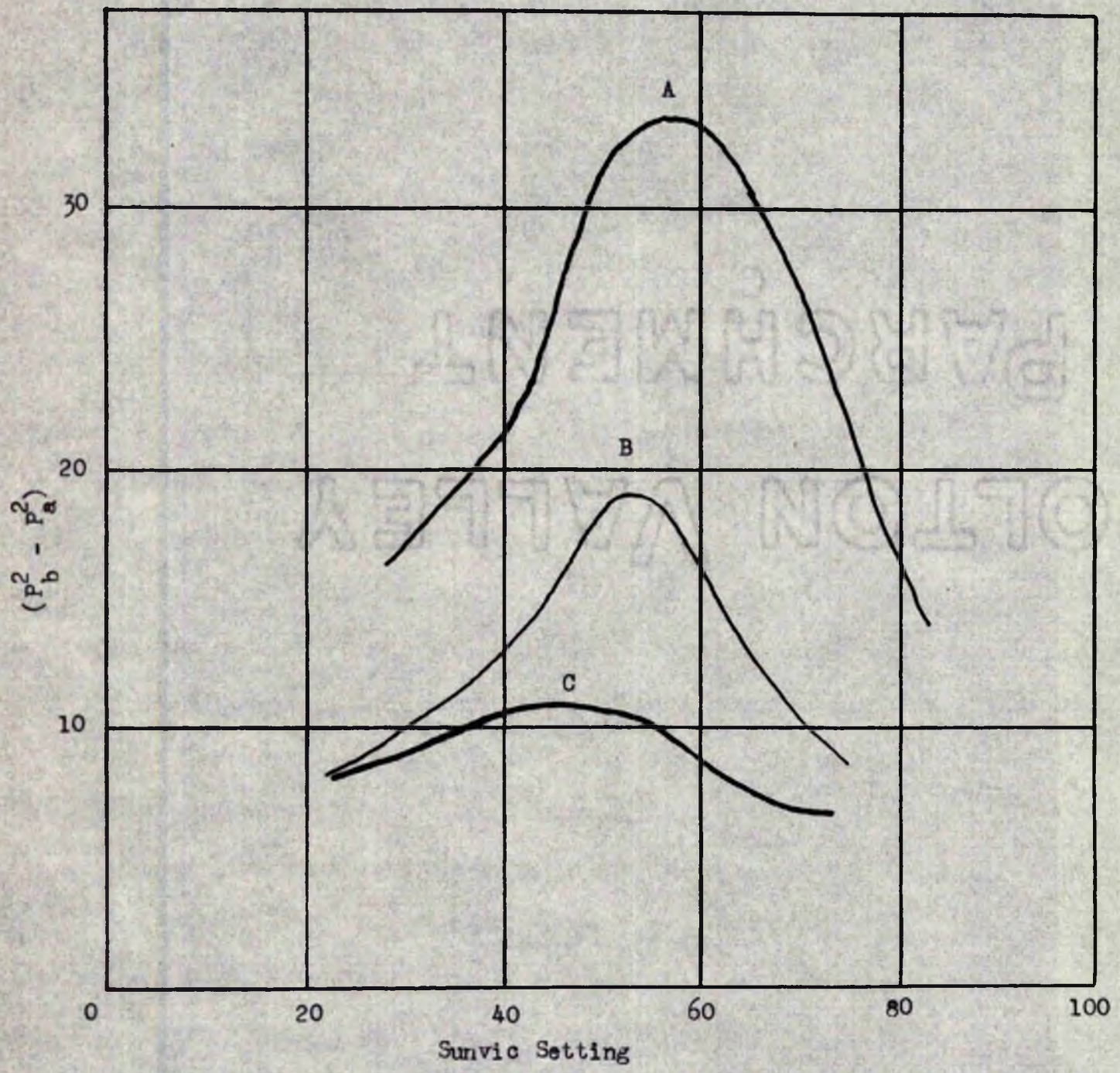
The Traps

The mixture of nitrogen, unreacted dibenzyl, and reaction products passed first through a trap, cooled by ice water, in which the dibenzyl and those reaction products which were solid at 0°C (e.g. stilbene) condensed. The remaining gases passed over to a liquid-air trap which removed the more volatile materials, leaving the nitrogen with any gases incondensible at liquid-air temperature, (e.g. hydrogen and methane). The re-entrant tube of the first trap was heated with a winding of "Nichrome" tape to prevent condensation of the solids in the narrow tube, and consequent restriction of the gas flow. Three sets of these traps were arranged in parallel to allow three experiments to be performed consecutively. The gas flow could be diverted from one set to another by electromagnetically operated grease free valves. See Figure 2.

The Circulating System

Figure 4.

Efficiency Curves for the Circulating Pump.



Curve A Static Pressure = 6.6 mm.
Curve B Static Pressure = 5.0 mm.
Curve C Static Pressure = 3.4 mm.

To circulate the carrier gas, a mercury diffusion pump having three jets in parallel was installed, the mercury boiler being heated by a Woods Metal bath wound with "Nichrome" tape and powered by a 200V. supply through a Sunvic Energy Regulator. Liquid-air traps before and after the pump removed any traces of contamination from the nitrogen stream, and prevented the passage of mercury vapour into the reaction vessel. As a further precaution, the gas passed through a "scrubber" before entering the saturator. This device removed any condensed spray by alternately heating the gas to 300°C and cooling to liquid-air temperature.

The optimum working conditions were determined by calibrating the pumping performance against the bath temperature for a range of carrier gas pressures. It was found that, on increasing the bath temperature, the rate of pumping increased to a maximum and then gradually fell off. The form of the curve obtained by plotting pumping rate against temperature was similar for all pressures, though the position of the maximum varied. Figure 4 shows the variation of output pressure related to the setting of the Sunvic Regulator. Thereafter, the pump was operated at that temperature corresponding to maximum pumping rate, in order that

any variation in mains supply and hence in bath temperature, would produce the minimum variation in cycling conditions.

The Flow Capillary

In order that the partial pressure of the reactant, and the time of its passage through the furnace, could be determined, the rate of flow of the carrier gas had to be measured. This was done by determining the pressure drop across a length of capillary tubing placed in the return line of the cycling system.

By applying Meyer's modification of Poiseuille's Law, the rate of flow could be determined.

$$n = \frac{\pi r^4 (P_b^2 - P_a^2)}{16.\eta.l.RT}$$

Where n = rate of flow in moles/sec.

r = radius of capillary in cm.

l = length of capillary in cm.

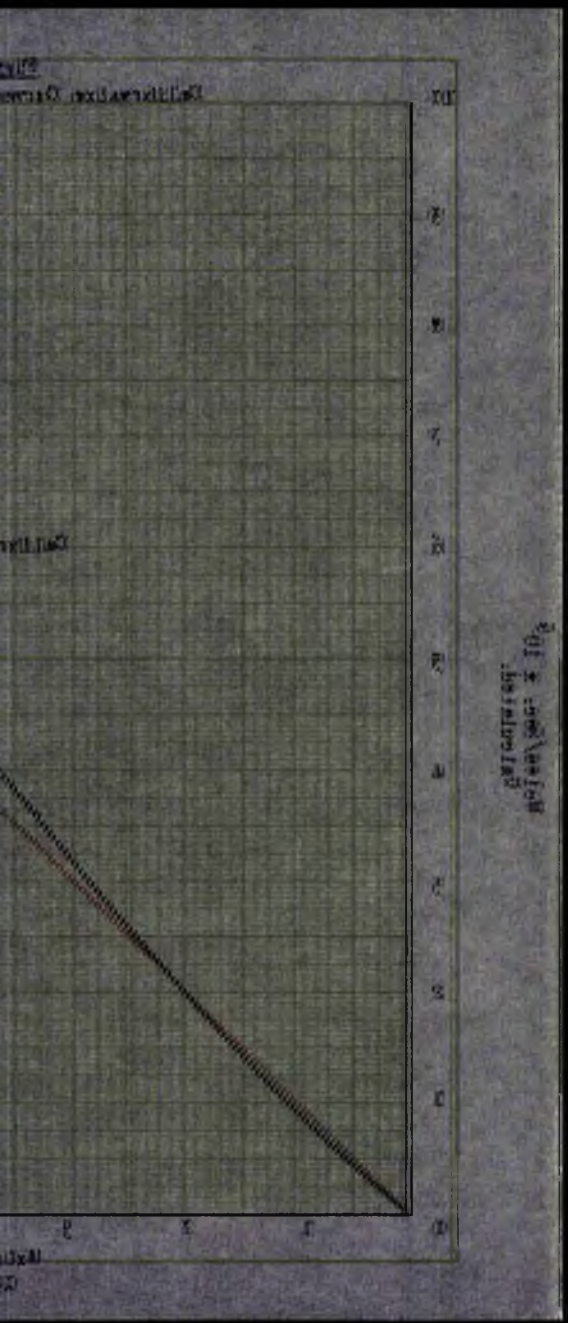
P_b and P_a = pressure before and after the capillary

η = viscosity of nitrogen in Poises.

R = gas constant.

T = absolute temperature.

It has been shown by C.B. Cowan that, at the low pressures used in the present work, Meyer's equation does not hold, and for accurate work the capillary had



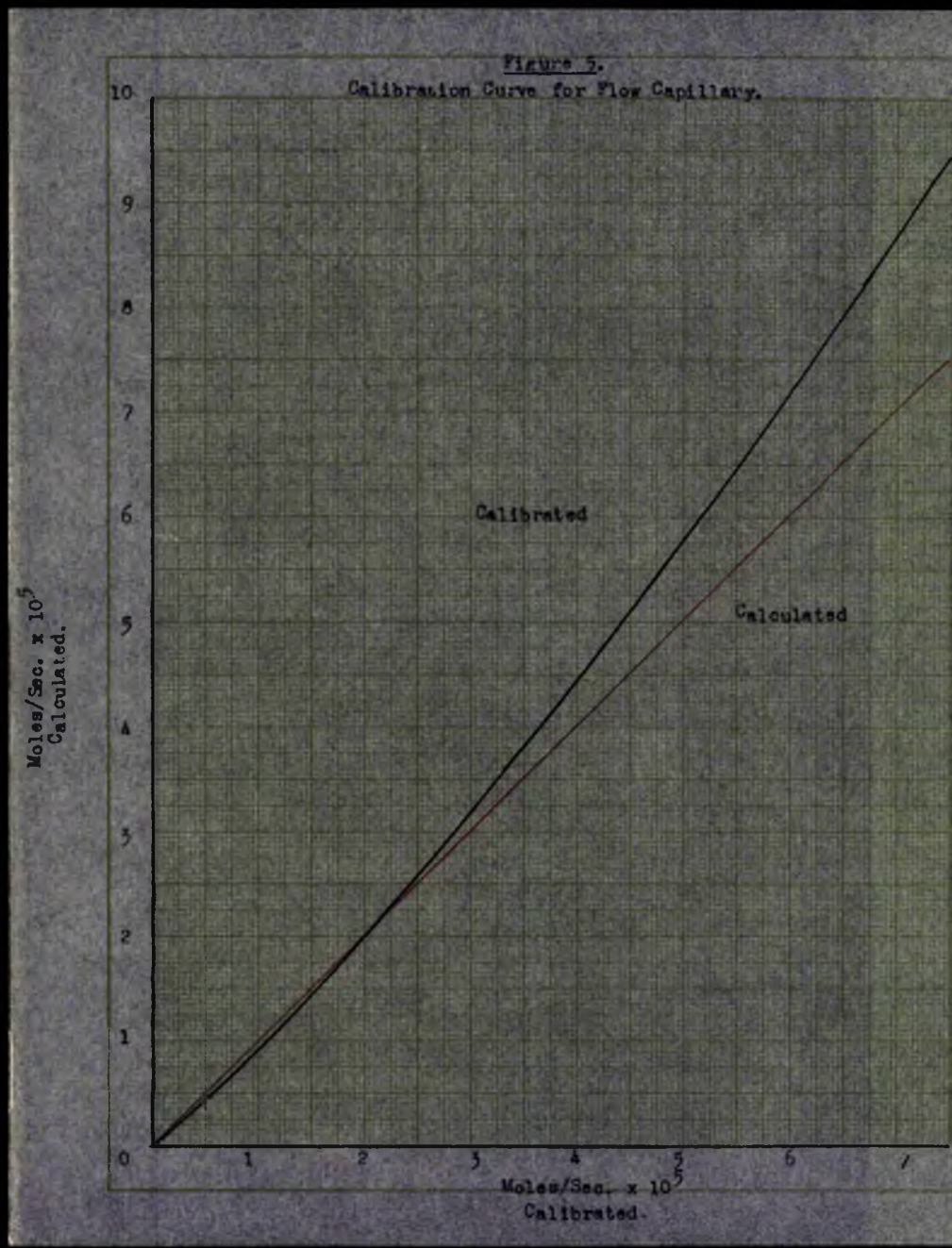


Figure 5.
Calibration Curve for Flow Capillary.
Moles/Sec. x 10^5 Calculated.
Calibrated
Calculated
0
1
2
3
4
5
6
7
8
9
10
Moles/Sec. x 10^5 Calibrated.

to be calibrated experimentally. The capillary used in the present work was one calibrated earlier by Cowan, and the divergence of the true rate from that obtained by calculation is shown in Figure 5.

For the determination of the fore and after pressures, twin McLeod gauges were built, the closed capillaries and compensating tubes being taken from a single length of uniform bore soda glass tubing.

In addition to the pressure drop across the capillary, it was necessary to determine the pressure of nitrogen inside the furnace in order that the concentration of dibenzyl could be determined. A McLeod gauge could not be placed at the furnace entrance during an experiment as the dibenzyl would have condensed in the cold gauge, so it was necessary to calibrate the flow in such a way that the pressure in the furnace could be correlated with that at some point where condensibles were not present. Accordingly the twin McLeod gauges were attached through two-way taps to points A and B immediately before and after the reaction vessel, and to a point C between the circulating pump and the "scrubber", this being the nearest suitable position for the permanent attachment of a gauge in the high pressure side of the system. Various pressures of nitrogen (3 - 6 mm.) were circulated, and the pressures

on either side of the flow capillary and at points A, B, and C, were noted. The pressure inside the reaction vessel was taken as the mean of A and B, and this was found in all cases to be greater than the pressure before the capillary by 2/3rds of the difference between that fore pressure and the pressure at C. During experiments, the pressures at the capillary and at C were measured, and from these the rate of flow and furnace pressure were calculated. After the calibrations had been completed, the gauges were detached from points A and B and the lines from the saturator to the furnace inlet and from the furnace outlet to the traps were wound with "Nichrome" tape and heated to 100°C to prevent condensation of the reactant and products. All ground joints in the heated lines were sealed with "Polythene" wax as this was found to be the most durable sealing compound at elevated temperatures.

The Vacuum System

A single stage mercury diffusion pump, backed by a Speedivac rotary oil pump with a liquid-air trap to collect volatile compounds, comprised the evacuating system, allowing the apparatus to be pumped down to 10^{-5} mm. Hg. A McLeod gauge capable of reading to 10^{-6} mm. and a Pirani gauge were added for pressure

determinations and leak testing respectively.

The Carrier Gas

Cylinder nitrogen was purified by allowing it to stream slowly, first through a liquid air trap, and then through two traps containing molten sodium. It was stored in three 5 litre reservoirs until required.

The Reactant

B.D.H. dibenzyl was purified by several recrystallisations followed by reduction to eliminate traces of stilbene. Reduction was repeated until no trace of stilbene could be observed in its ultraviolet absorption spectrum.

Operating Procedure

A charge of dibenzyl was placed in the saturator which was then attached to the apparatus with "Polythene" wax. The saturator was immersed in a bath of acetone/solid carbon dioxide, taps T1, 3, 4, and 5 opened, T2 closed, and the whole system evacuated. T5 was then shut, and nitrogen from one of the reservoirs introduced to a suitable pressure (5mm.). T2 was closed, the electromagnetic cut-off lifted, and the heaters to the circulating pump, the furnace inlet and outlet lines, and the "scrubber" switched on. The furnace itself was connected through a time switch which closed automatically in the early morning and had reached a

stable temperature before the experiment began.

Dewar flasks containing liquid-air were placed round trap Tr 2, the traps before and after the circulating pump, and the "scrubber", while ice water was placed round Tr 1. When the circulating pump had reached equilibrium, the acetone/carbon dioxide bath surrounding the saturator was replaced by a thermostatically controlled oil bath at a suitable temperature ($70^{\circ}C$ - $90^{\circ}C$), and a stop watch started. Pressure readings at all three points were noted at intervals of a few minutes, and the furnace was maintained at a constant temperature by manual adjustment of the "Variac" autotransformer. When a sufficient quantity of products had been collected (normally 15 - 30 minutes were required), the gas flow was diverted from the first set of traps to the second, and after a similar period, to the third. When the run had reached its time limit, the acetone/carbon dioxide bath was replaced. All heaters were switched off, and air admitted. The products could then be collected from the traps Tr. 1 and Tr. 2.

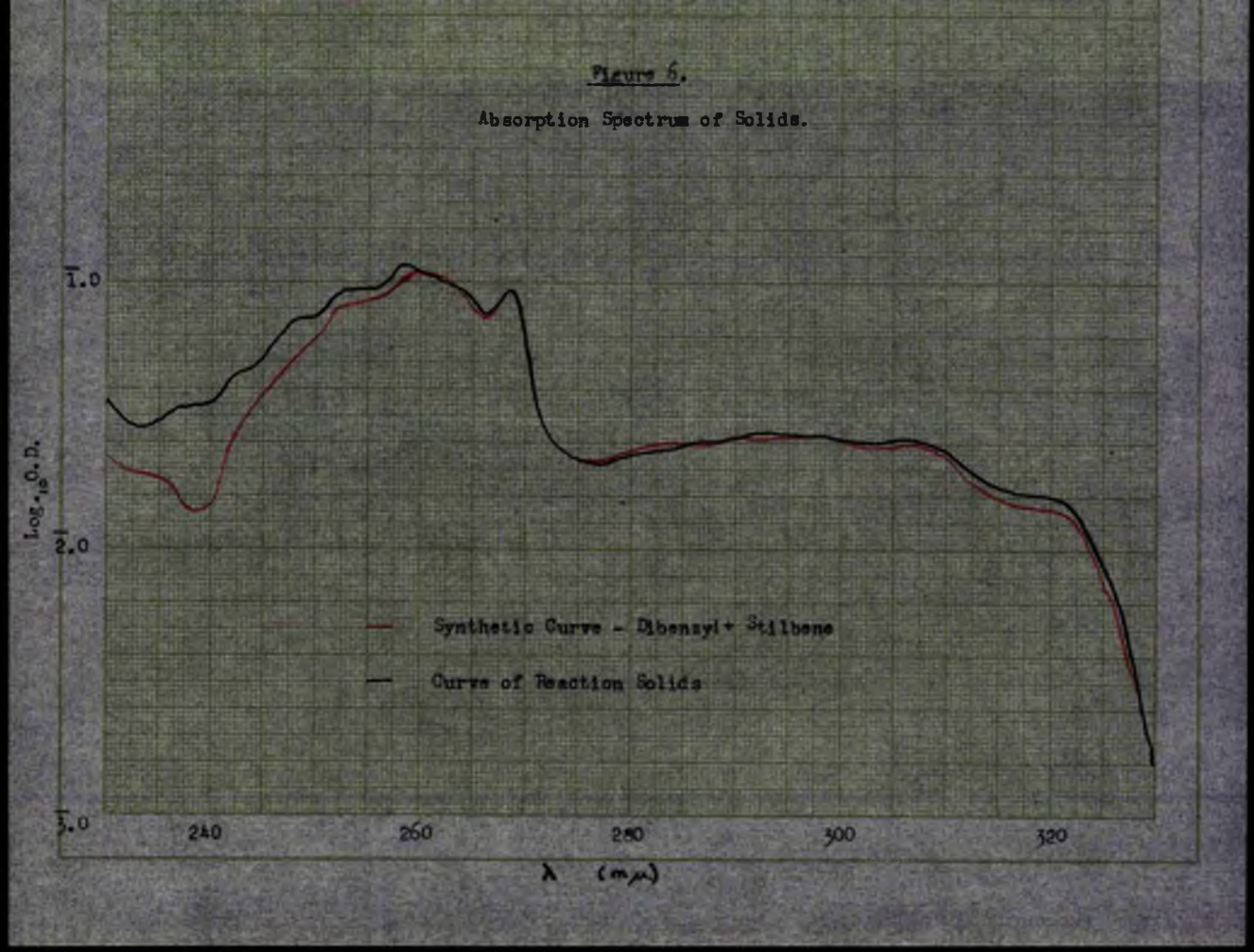
The Reaction Products

(a) The Solids

The solid products reported by Miles were

Figure 6.

Absorption Spectrum of Solids.



unchanged dibenzyl, and a small quantity of stilbene. Graebe (54), pyrolysing at atmospheric pressure, found phenanthrene to be present, while Meyer and Hofmann (55) claimed a considerable proportion of anthracene. It was intended, therefore, to investigate the possible existence of any or all of these in the products mixture.

The most promising line of investigation was the examination of the ultraviolet absorption spectrum of the mixture. All the hydrocarbons mentioned above have distinctive absorption spectra in the region 200 mμ. - 400 mμ., and the presence of each in a mixture could be readily detected.

Most compounds obey Beer's Law of light absorption, which can be written:-

$$I = I_o 10^{-Ecd}$$

where I_o = incident light intensity.

I = transmitted light intensity.

E = extinction coefficient.

c = concentration of the absorbing medium.

d = length of the light path.

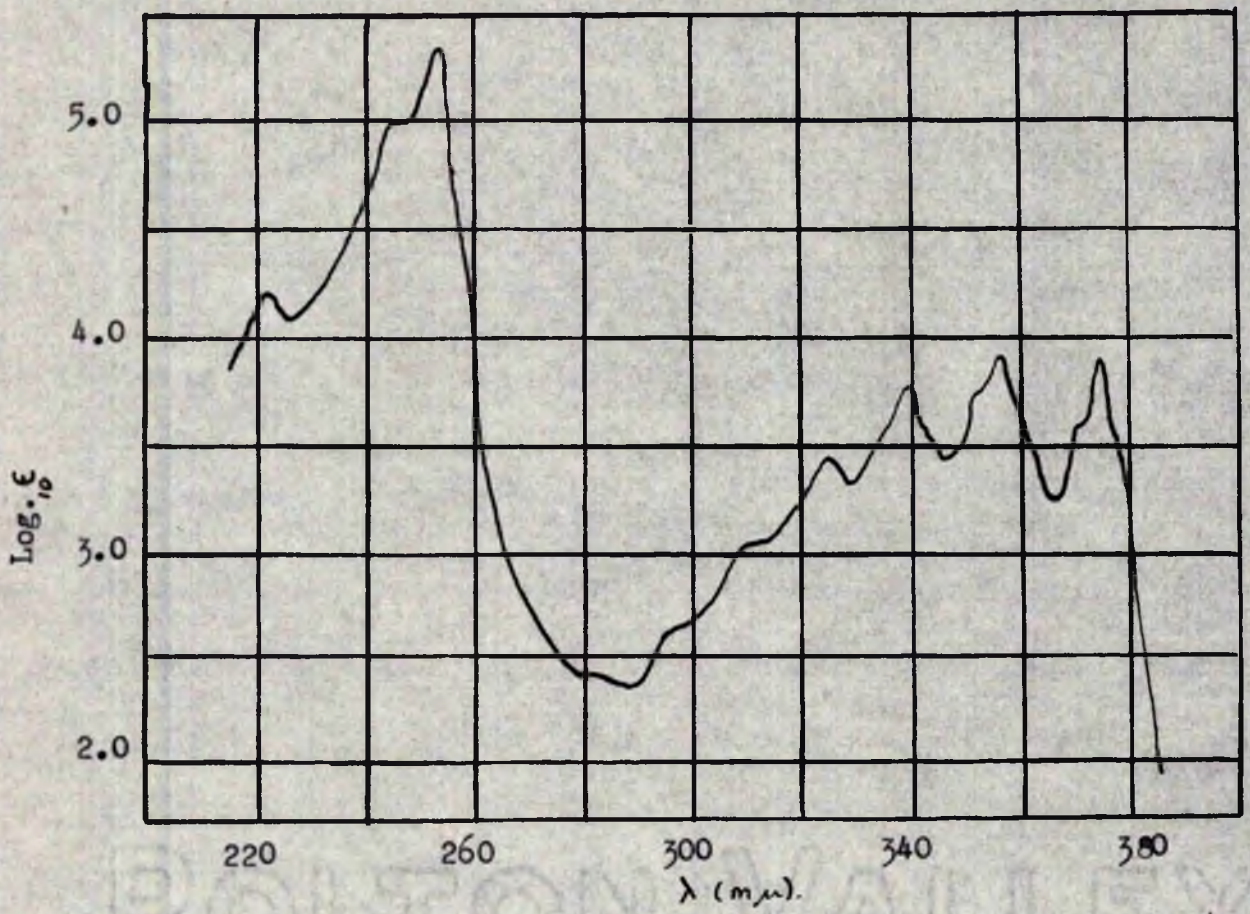
This is generally used in the form

$$Log_{10} I_o/I = Ecd = \text{Optical Density (O.D.)}$$

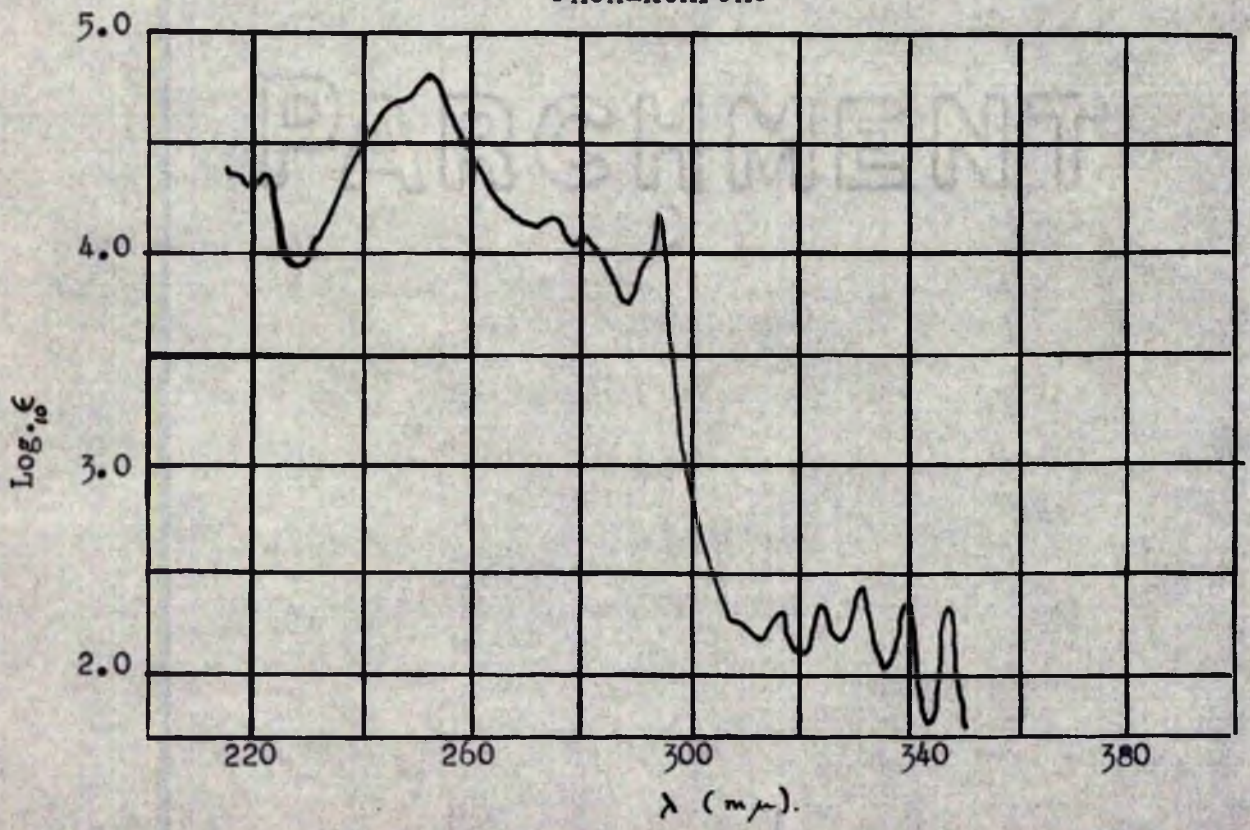
With a mixture, optical density is usually

Figure 7 (a)

Anthracene



Phenanthrene



linearly additive. Thus at a particular wavelength,

$$O.D._{observed} = O.D._1 + O.D._2 + O.D._3 + \text{- - - - - +} O.D._n$$
$$= E_1c_1 + E_2c_2 + E_3c_3 + \text{- - - - - +} E_nc_n$$

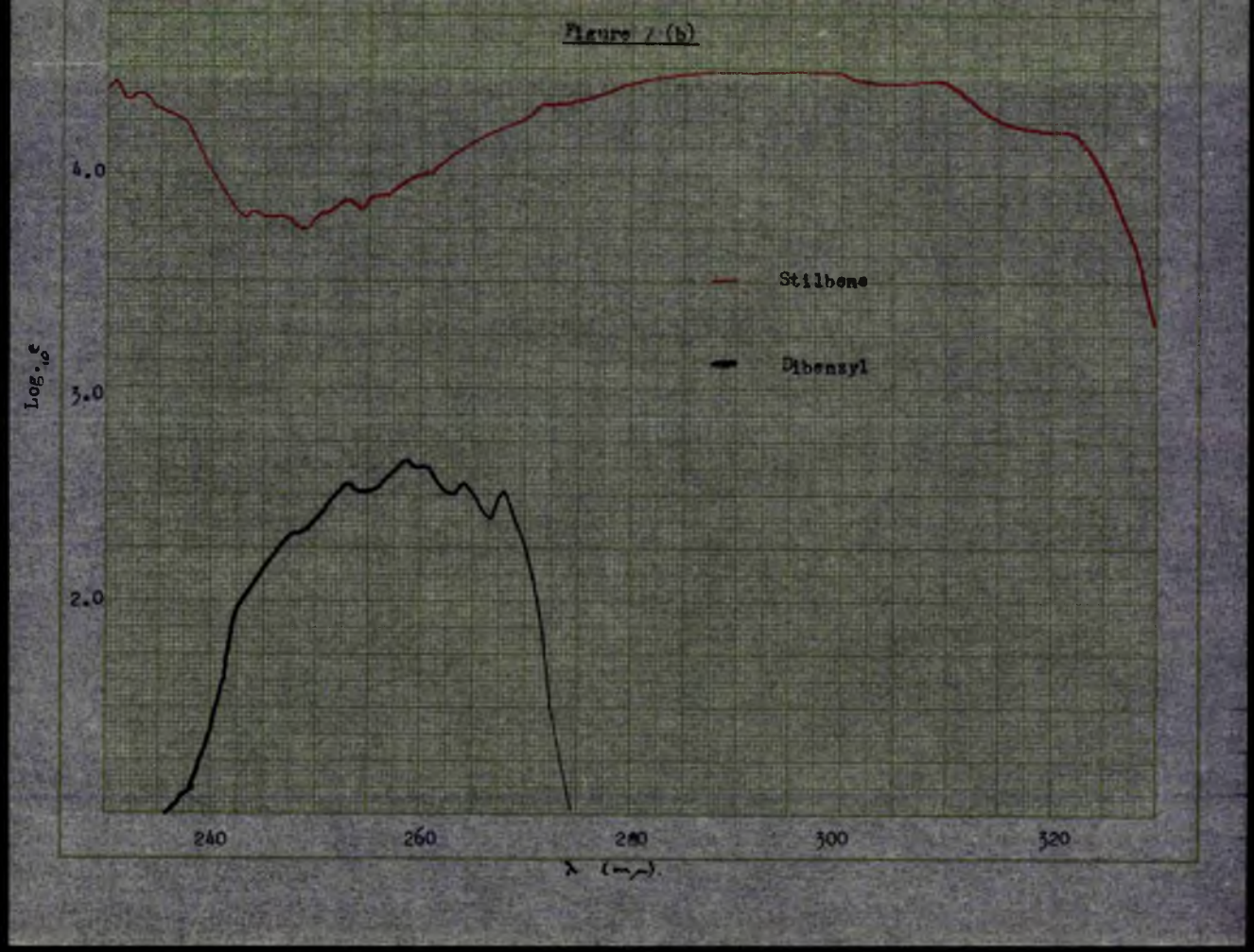
where $E_1, E_2, E_3, \text{- - -} E_n$ are the extinction coefficients of the pure components, and $c_1, c_2, c_3, \text{- - -} c_n$ their concentrations. Hence, if the values of E are known for the n components, and the composite O.D.s measured for n suitable wavelengths, the concentrations of the components can be calculated by solving the n simultaneous equations. To obtain the appropriate values of E, calibrations are necessary using known concentrations of the pure components.

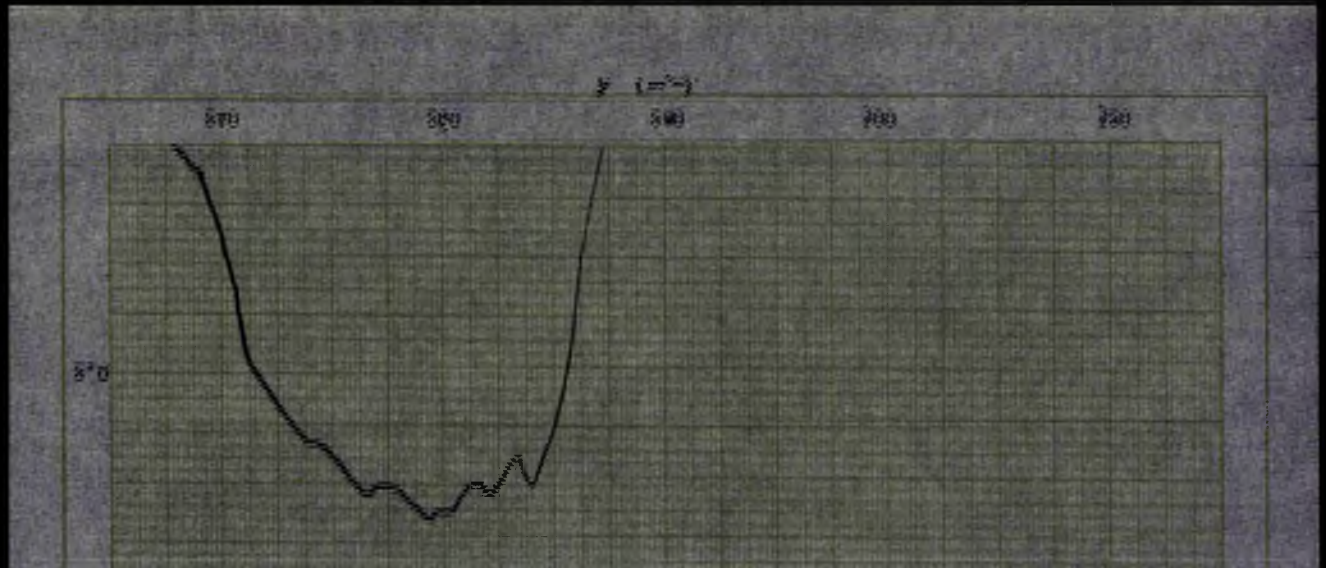
Characterisation

The contents of trap Tr. 1 were dissolved in methanol which had been distilled over activated charcoal to remove any strongly absorbing impurities. Several methods were tried, and this was found to give the greatest transparency.

The absorption of the mixture was determined on a "Unicam" single beam quartz spectrophotometer Model S.P.500, from 200 mμ. to 400 mμ. at intervals

Figure 1 (b)


4.0
3.0
2.0
Log.ε
Stilbene
Dibenzyl
240
260
280
300
320
λ (mμ).


ν̄ (cm⁻¹)
3700
3600
3500
3400
3300
3.0

of 1 mμ. using, for the solvent compensating cell, a sample of methanol from the same batch as that used to dissolve the products. The cells were of quartz, having a light path of 1 cm. Slit width was maintained at 0.2 mm. throughout. Figure 6 shows the optical density of the mixture plotted against wavelength in millimicrons.

Figure 7 shows a plot of the extinction coefficients of all the anticipated components against wavelength. The anthracene and phenanthrene curves were taken from the literature (56). The dibenzyl and stilbene curves were constructed from calibrations performed on pure samples. These samples were weighed accurately on a micro-balance, dissolved in methanol in a 100 ml. standard flask, and scanned on the spectrophotometer. Six samples of each were prepared, and their extinction coefficients averaged for each wavelength.

The products graph shows clearly the characteristic structure of dibenzyl in the region 240 mμ. - 270 mμ. The absorption between 280 mμ. and 330 mμ. resembles closely the spectrum of stilbene. Of anthracene and phenanthrene, which absorb very strongly at 252 mμ. there is no trace. Moreover, both of these compounds exhibit a series

Table 2

λ (mμ)	ϵ. Stilbene	ϵ. Dibenzyl
320	1.60×10^4	-
268	1.58×10^4	3.17×10^2

of characteristic peaks at wavelengths longer than 330 mμ., while the mixture curve is transparent beyond this value. It would appear, therefore, that neither anthracene nor phenanthrene is a product of the thermal decomposition of dibenzyl under the conditions employed in this investigation.

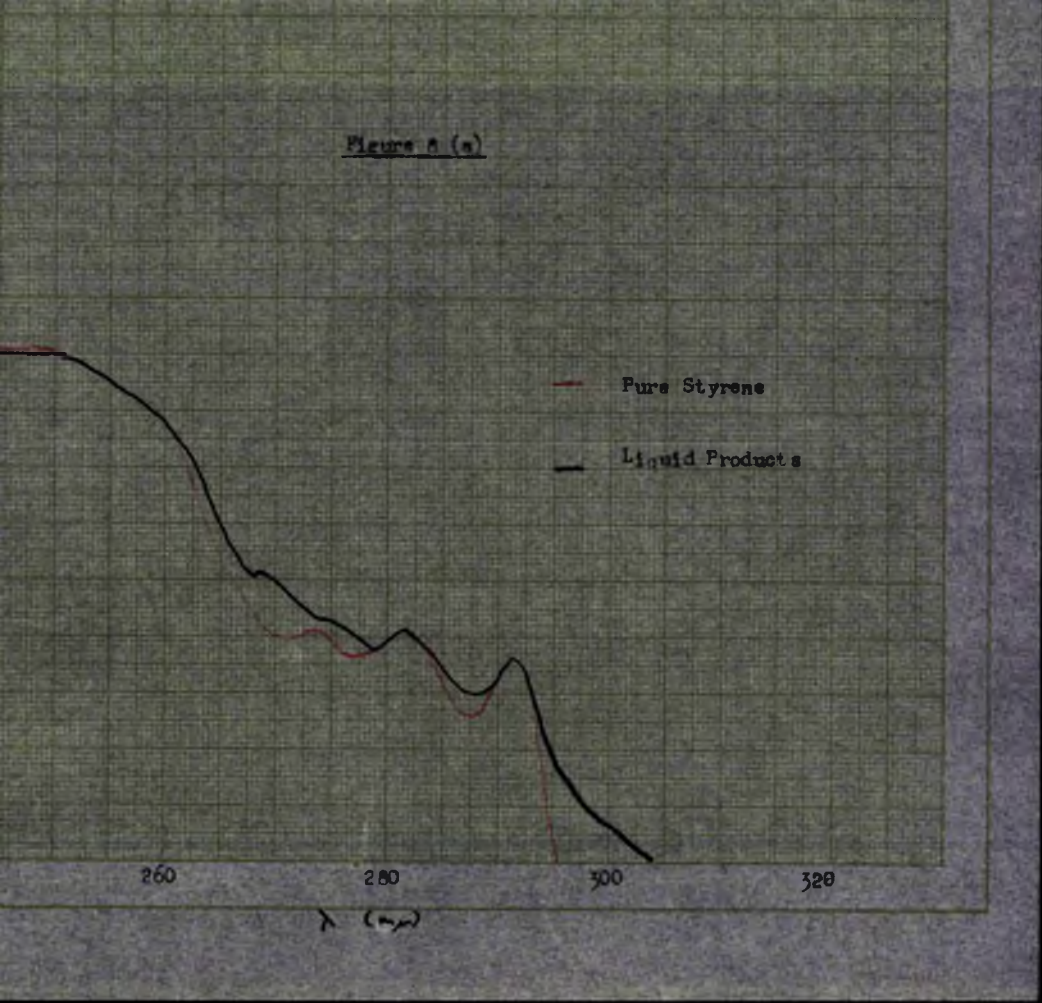
Also included in Figure 6 is a synthetic curve constructed from the estimated concentrations of dibenzyl and stilbene in the mixture. It can be seen that the two curves correspond very closely in the higher wavelength region, but diverge appreciably for wavelengths lower than 250 mμ. The accuracy of measurement in this region was so poor that it was not possible to obtain, by subtraction, a satisfactory absorption curve from which to identify the unknown material, but from the general position of the absorption band, it is likely that this was due to isomers of dimethyl diphenyl. If so, the concentration of these in the mixture would be minute, as dimethyl diphenyls have very high extinction coefficients in this region, and so they can be neglected in any consideration of the principal reactions.

Quantitative Estimation

By making use of the linear additivity of

1.0
0
1.0
240

Figure 8 (a)


Pure Styrene
Liquid Products
260
280
300
320
λ (mμ)


λ (mμ)
260
280
300
320

optical densities, it is possible to estimate the absolute concentrations of the components of the solids mixture. In the present case, the absorption spectra of dibenzyl and stilbene, and their relative concentrations, were well suited to this form of analysis. Firstly, the maximum extinction coefficient of stilbene is greater than that of dibenzyl by a factor of 50, while their concentrations were in the ratio of roughly 1 in 100. Hence the contributions of the two components to the observed optical density were of the same order, and their concentrations could be estimated to the same degree of accuracy. ($\pm$ 1%) Moreover, as the strongest absorption band of stilbene occurs in the region where dibenzyl is transparent, the concentration of stilbene could be measured directly, and its contribution to the optical density at some wavelength where dibenzyl absorbs could be deducted.

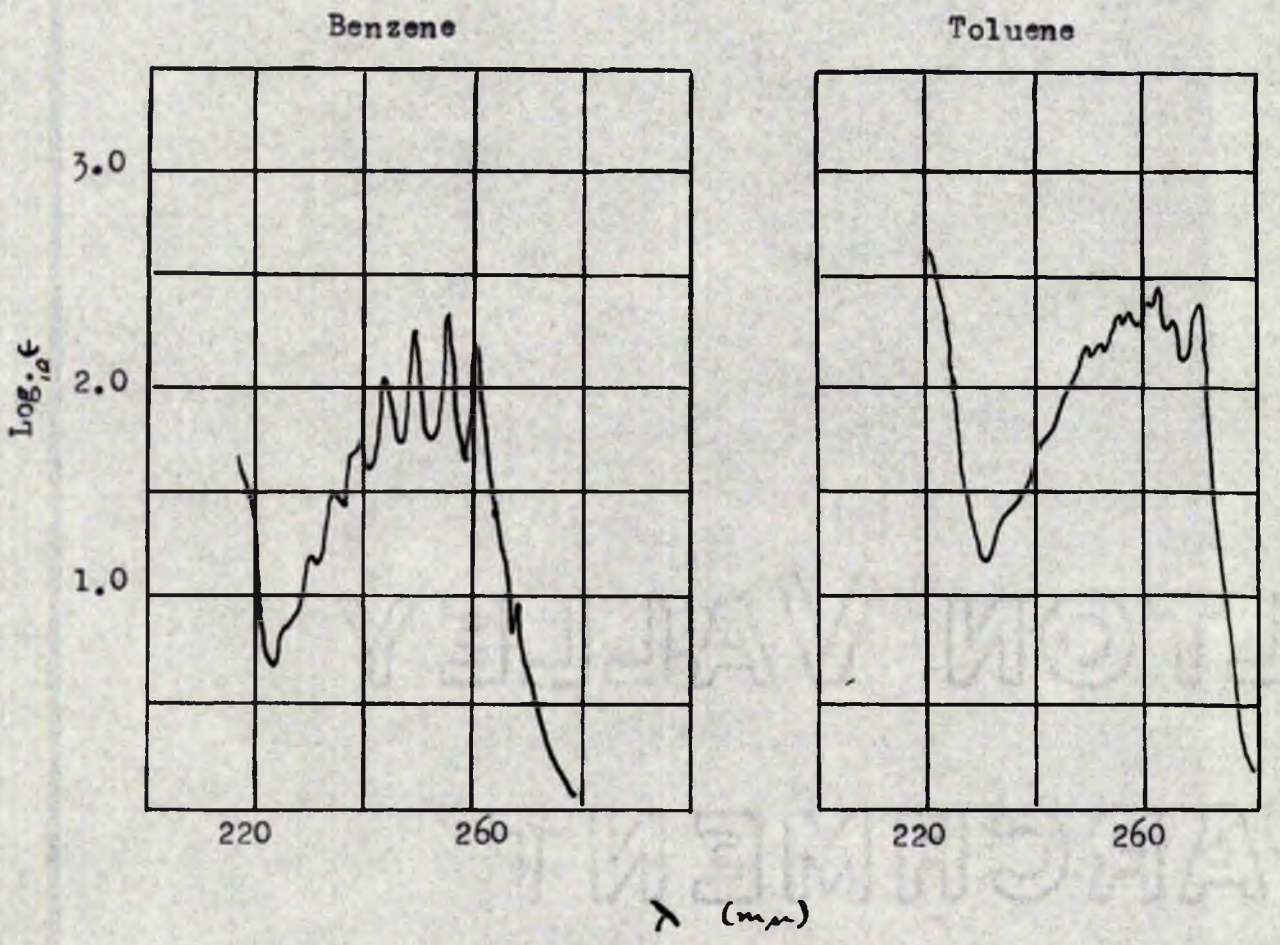
For the present work the O.D.s at 320 mμ and 268 mμ. were determined for the solids from each run, and the concentrations calculated using the 'E' values shown in Table No. 2.

(b) <u>The Liquids</u>

From Graphs (8a) and (8b), it is obvious

Figure 8 (b)

Ultra-Violet Spectra



that little is to be gleaned from the absorption data of the products from trap Tr.2. The mixture scan, apart from one small peak at 268mμ. shows the characteristic spectrum of styrene which completely masks the absorption due to the other products, viz. benzene and toluene. The contribution of toluene is apparent at 268mμ. only, and its magnitude is such that accurate estimation of its concentration in the mixture is impossible. The presence of benzene is not detectable. It was necessary, therefore, to develop some other system for the analysis of these compounds.

Mass Spectrometry

For the analysis of these volatile aromatics, the use of mass spectrometry seemed possible, unless the overlapping of fragment patterns proved excessive. Electron bombardment of complicated molecules causes not only ionisation, but also dissociation to many fragments, the ions of which appear in the mass spectrum, and can, as is the case with toluene, occur in greater quantity than the ions of the parent. Table 3 , taken from the Mass Spectral Data published by the American Petroleum Research Institute, shows the

Table 3

m/e	Styrene	Toluene	Benzene
104	100	-	-
91	0.01	100	-
78	32.2	0.14	100

contributions of styrene toluene and benzene to the m/e values of 78, 91 and 104. The only appreciable fragment peak for these values is that contributed by styrene to m/e = 78. The fragment at m/e = 91 is negligible, and could not seriously affect the toluene contribution, the largest peak of which occurs at this value.

The Mass Spectrometer

The instrument available for this work, a copy of that designed by Nier (57) was built in the department.

The sample is streamed at pressures of 10^{-4} mm. into the ionisation chamber, where it passes at right angles through a beam of electrons. The resulting positive ions are withdrawn from the chamber through a slit by a small negative potential applied to a plate immediately below. They are then accelerated by a potential drop of 1800 - 2000 volts, and enter the magnetic field where they are deflected through an angle which depends on their mass and charge. Those which are correctly aligned pass through a further slit and impinge on the collector plate. The resultant ion current passes down a resistor of 10^{11} ohms and the potential drop across this is recorded on a

Figure 9

Sample Handling System

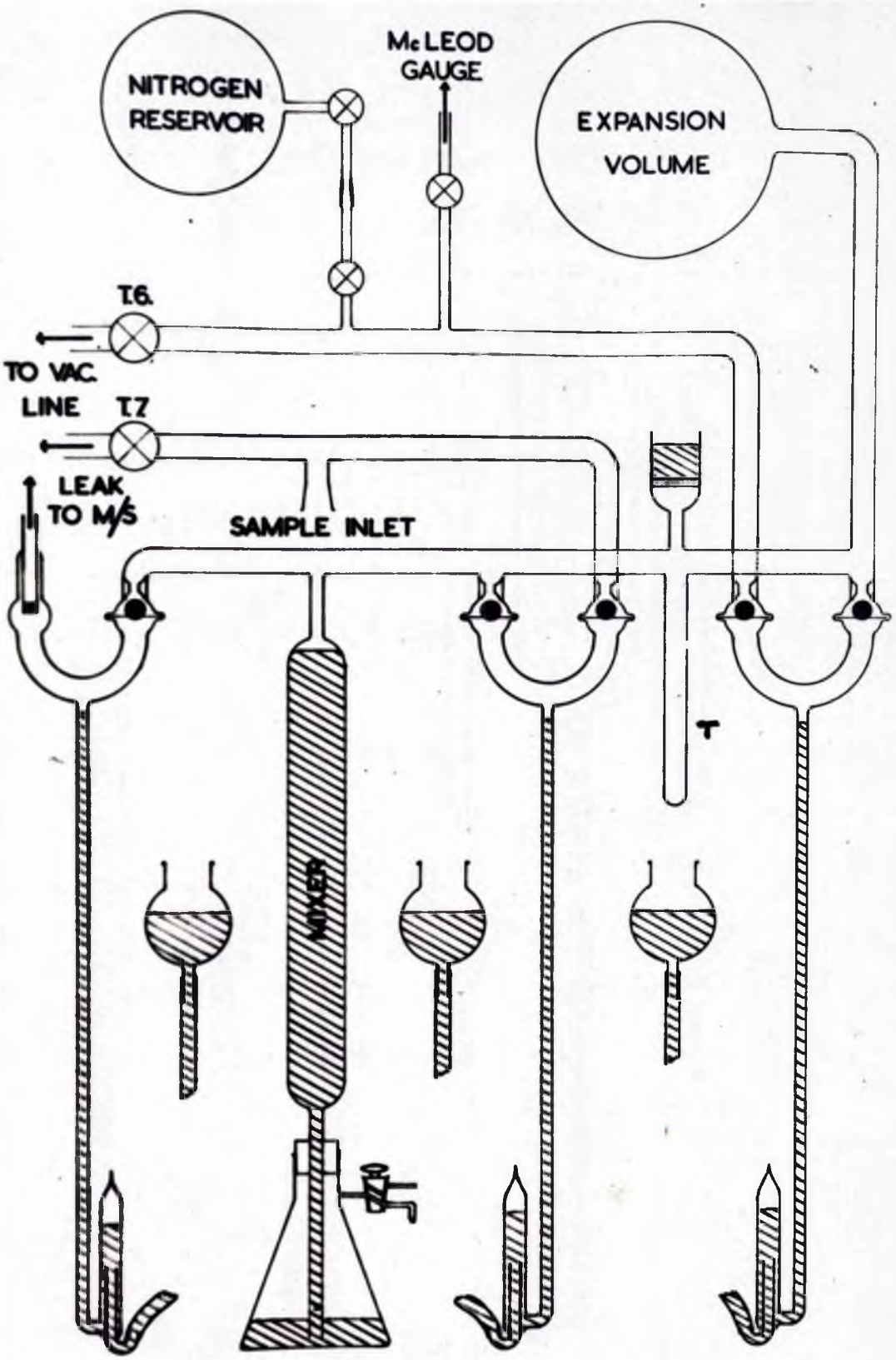


chart. By varying either the magnetic field or the accelerating voltage, ions of different m/e ratio can be directed in turn on to the collector plate, and a measure of their intensities obtained.

The Sample Manifold

A five litre expansion reservoir was coupled to the gas inlet of the mass spectrometer through a 'Metrosil' 4F porous plug 4mm. long. It had been shown that this form of leak admitted a satisfactory pressure of sample to the ionisation chamber with a pressure of 2 - 3 mm. in the manifold, Figure 9. Mercury cut-off valves were used in place of taps to avoid loss of products by absorption in tap grease. The original cut-offs employed small glass cones fitting into ground sockets, but these were found to remain in their seatings when the mercury was lowered, and could be dislodged only after vigorous tapping. Moreover, the space occupied by the cone when lowered was so large that the rate of evacuation was exceedingly poor. Consequently, other methods were investigated, and the design illustrated in Figure 9 was adopted. In place of the conical floats, ½ in. rustless steel balls seated in ground glass sockets were employed. The seatings were

ground in the laboratory with a similar steel ball brazed on to a steel rod as a grinding tool, using several grades of carborundum powder as the grinding agent. When complete these valves could sustain a pressure of one atmosphere without any leakage of mercury between the ball and its seat.

During early calibrations it was discovered that some device was needed for mixing the gaseous components in the manifold. If a mixture of volatiles was condensed in the side tube T and vaporised several times, the ratio of the peak heights of the principal ions varied considerably, and depended on the rate of volatilisation of the condensate. To agitate the mixture, a mercury column displacing 1 litre, attached near the porous plug, was raised and lowered several times.

For the admission of calibration samples, a mercury sealed sintered disk was used (59). Several micropipettes of the self filling type were constructed and tested, but were discarded as unsatisfactory. The pipettes did not readily deliver the whole of their charge, and the quantity admitted could not be varied without changing the pipette. A method of weighing small

samples in capsules on a microbalance and breaking these in the manifold proved too clumsy for extensive investigations, though it was employed to estimate the accuracy of other methods.

An 'Agla' brand micrometer syringe was obtained, and the reliability of its delivery through the sinter determined. It was found to be capable of delivering 0.01 ml. to within ±0.5% in normal use. The vacuum on the sinter tended to withdraw slightly more than the measured amount, though this seldom exceeded 0.0001 ml. which was well within the accuracy of the mass spectrometer.

Calibration

(a) Reproducibility

The response of the mass spectrometer to m/e = 78 was studied for a series of 0.01 ml. samples of pure benzene. The results obtained varied by as much as 20% over eight runs, though later samples showed more consistency than the first. The day to day variations were even more widely divergent. A few runs were performed using weighed capsules and these also showed considerable variation, indicating that the

fault did not lie in the delivery of the sample by the syringe. A 3 litre reservoir of pure nitrogen, and a McLeod gauge were added to the system and several 2 mm. samples of nitrogen admitted to test the reproducibility of the 28 peak. This was found to vary slightly if nitrogen alone was used, though, when alternated with samples of benzene, wide deviations appeared. Comparison of the 28 and 78 values showed, however, that although the absolute values of the ion currents varied considerably, the ratio of 78 to 28 remained fairly constant. Thus if a 0.01 ml. sample of benzene was admitted, its 78 value noted, the vapour condensed in the side arm, and the 28 value of 2 mm. of nitrogen found immediately after, the 78 / 28 ratio did not vary by more than one or two per cent. This technique was followed in all subsequent investigations. The values of the hydrocarbon peaks were referred to a sensitivity, the unit of which was defined as 10 volts 28 peak per mm. nitrogen in the manifold. Further consistency was achieved by condensing the sample in the

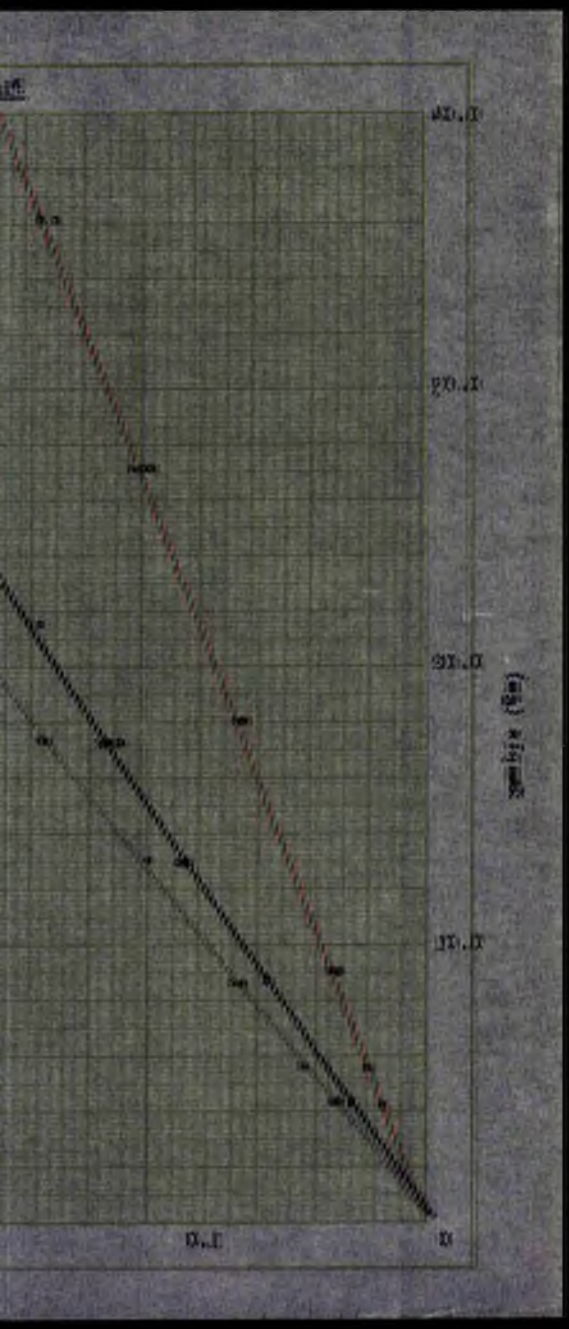
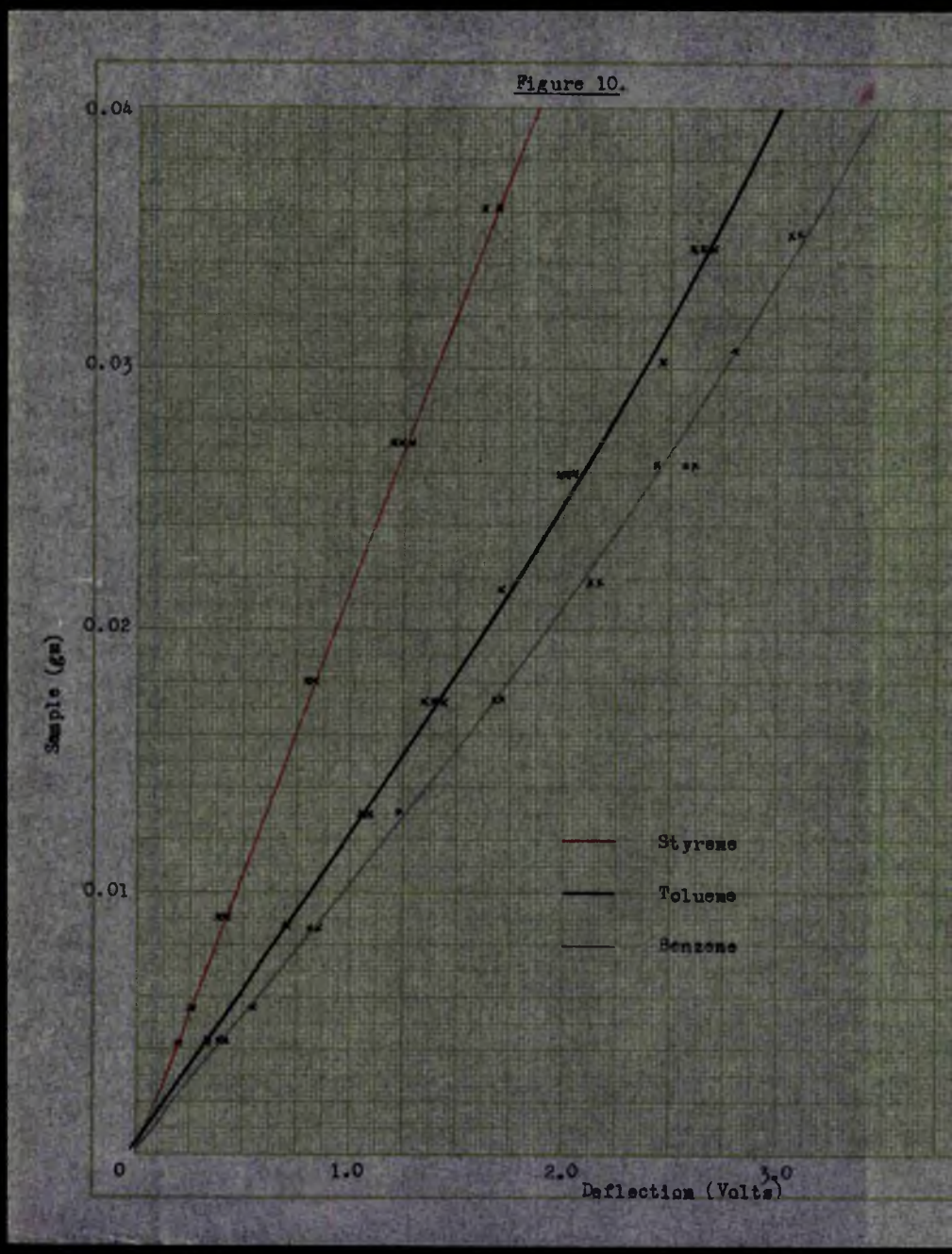


Figure 10.


0.04
0.03
0.02
0.01
Sample (gm)
0
1.0
2.0
3.0
Deflection (Volts)
Styrene
Toluene
Benzene

side tube on admission, before expanding into the reservoir, as some of the liquid tended to remain in the sinter.

(b) Linearity

The linearity of the instrument's response to nitrogen pressure had already been demonstrated by J.O. McCrae.

Figure 10 indicates the results obtained for benzene, toluene, and styrene over the range 0.005ml. to 0.045ml., the recorded voltage being referred to unit sensitivity. True linearity is not exhibited, though the deviation is not appreciable at low pressures.

(c) Mixtures

The accuracy of analysis of a mixture of these compounds using the pure hydrocarbon calibrations was checked by admitting a sample whose composition was known accurately. The results obtained were very much lower than was expected for styrene and toluene, slightly higher for benzene.

With the instrument recording the 104 peak, styrene was injected into the manifold, and the peak height noted. An equal

quantity of toluene was added and thoroughly mixed with the styrene. A drop of 20% in the 104 contribution resulted. Benzene was then added, resulting in a further decrease. This was repeated, recording 91 and 78 peaks respectively. Each component was found to have an influence on the various peaks of the others, causing depression of the 104 and 91 peaks, and a slight increase in the 78 peak which could not be accounted for by the fraction contributions of the other two.

That this effect was not confined to aromatic hydrocarbons was demonstrated using nitrogen and n-hexane, each of which affected other components, though not so strongly.

An attempt was made to calibrate this interference so that its effect could be allowed for in the analysis of unknown mixtures, but the required calculation was so complex, and the interference so variable, that this scheme had to be abandoned.

(d) Emission Variables

During the above work, drifts in the conditions in the ionisation chamber began to be observed, indicated by a slow increase in

the filament supply current, and a considerable drop in emission to the electron trap. The instrument incorporated an electronic regulator which automatically maintained a constant flow of electrons from the filament to its surrounding box by adjustment of the filament current. That part of the emission which passed through the collimating slit into the chamber, and was responsible for ionisation, was collected in a small Faraday cup and is termed below the trap current. The normal operating value of this current was 16 μA., and manual adjustment to this value on starting each day had till then been sufficient.

The effects which were manifested after several weeks' work on aromatics were:-

1. The admission of hydrocarbons caused a decrease in the number of electrons reaching the trap. 0.03 ml. of toluene lowered the current from 16μA. to 8μA.
2. Due to the emission stabiliser, the emission to the box remained constant, though the filament supply current rose to maintain it at the correct value.

3. On removal of the hydrocarbons, conditions return to normal.

4. The drop in trap current produced a corresponding drop in the recorded peak heights.

5. The magnitude of the effect increased with the pressure of the sample.

6. Styrene had a very much greater effect than toluene or benzene.

7. After flashing the filament in the presence of a sample the trap current returned to normal for a few seconds, then slowly dropped again.

8. Aliphatic hydrocarbons had a reduced effect, inorganic gases had none.

9. Allowing the spectrometer to run for several hours in continued contact with styrene produced the following result. The trap current dropped slowly until, after about 30 minutes, it reached a minimum of 2μA. It remained constant at this value for a further 20 - 30 minutes after which it rose gradually to 12μA. On evacuating the sample manifold, the reverse was observed, though the maximum

value was much less than 16μA.

One possible explanation of these phenomena would be the adsorption of hydrocarbon on the slit edges of the ionisation chamber, causing the potentials between the electrodes to change. Another possibility is the formation of a carbide layer on the filament surface. As the temperature of the filament is not uniform throughout its length, heat being conducted away from the ends by the thick leads, carbide formation would be a maximum at the centre of the tungsten strip. If a carbide coated surface has a reduced emissivity for electrons this would account for the fall in trap current. Prolonged exposure would result in the extension of the carbide layer to the cooler portions of the filament, lowering the emissive power of the whole strip. On evacuating the manifold, the carbide would be gradually removed by traces of water vapour present in the tube.

That this effect does in fact occur was shown by streaming oxygen through the ionisation chamber after the filament had

been subjected to hydrocarbon treatment for several hours. The rate of change of trap current was greatly increased, and eventually returned to the original value of 16μA.

Replacement of the filament, and cleaning of the chamber assembly returned the instrument to a state of consistent emission conditions for 2 - 3 weeks, after which hydrocarbons depressed the trap current once more. It is possible, therefore, that both effects existed, though only the carbide formation could be countered without the lengthy task of removing and cleaning the spectrometer head.

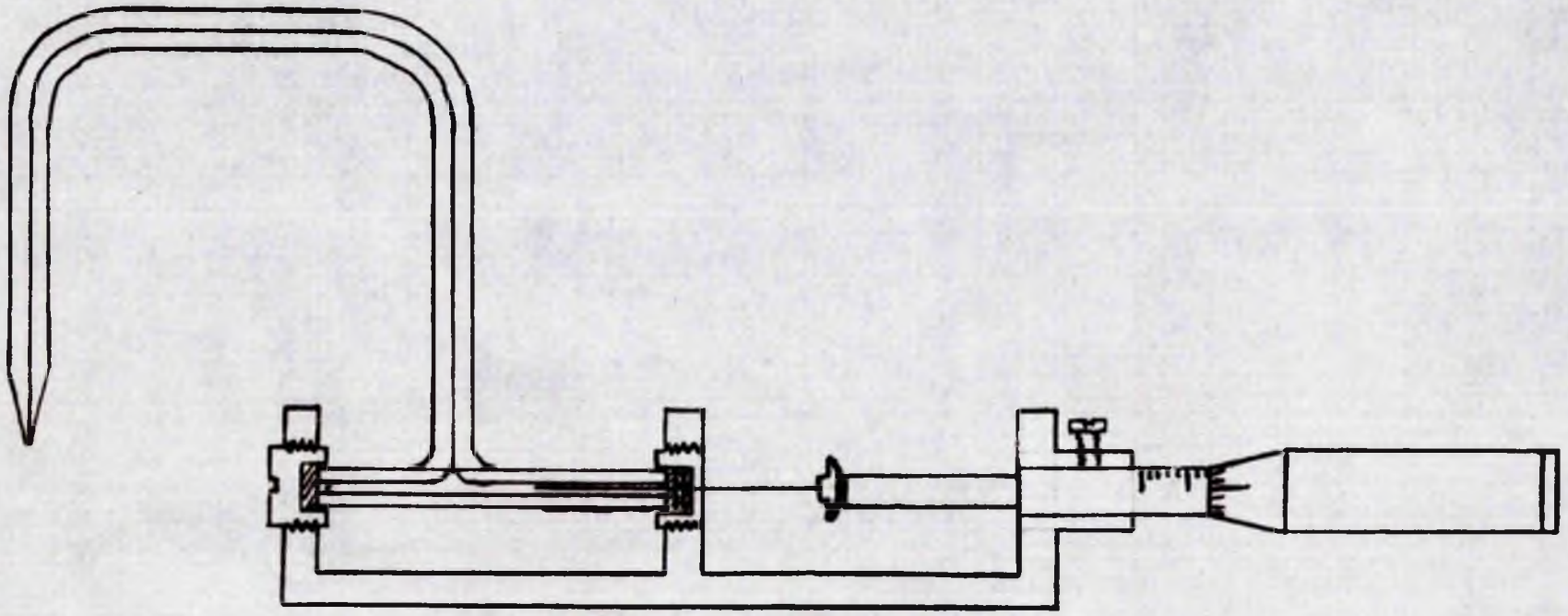
By considerably reducing the sample pressures, (not more than 0.02 ml.) of mixture), trap variations were kept at a minimum, and the slight variations during an analysis were compensated by manual adjustment of the emission controls. Provided the trap current was maintained at a constant value, the reproducibility obtainable was of the order of 1%.

Microburettes

As has already been stated, the interferences

FIGURE 11

MICROBURETTE.

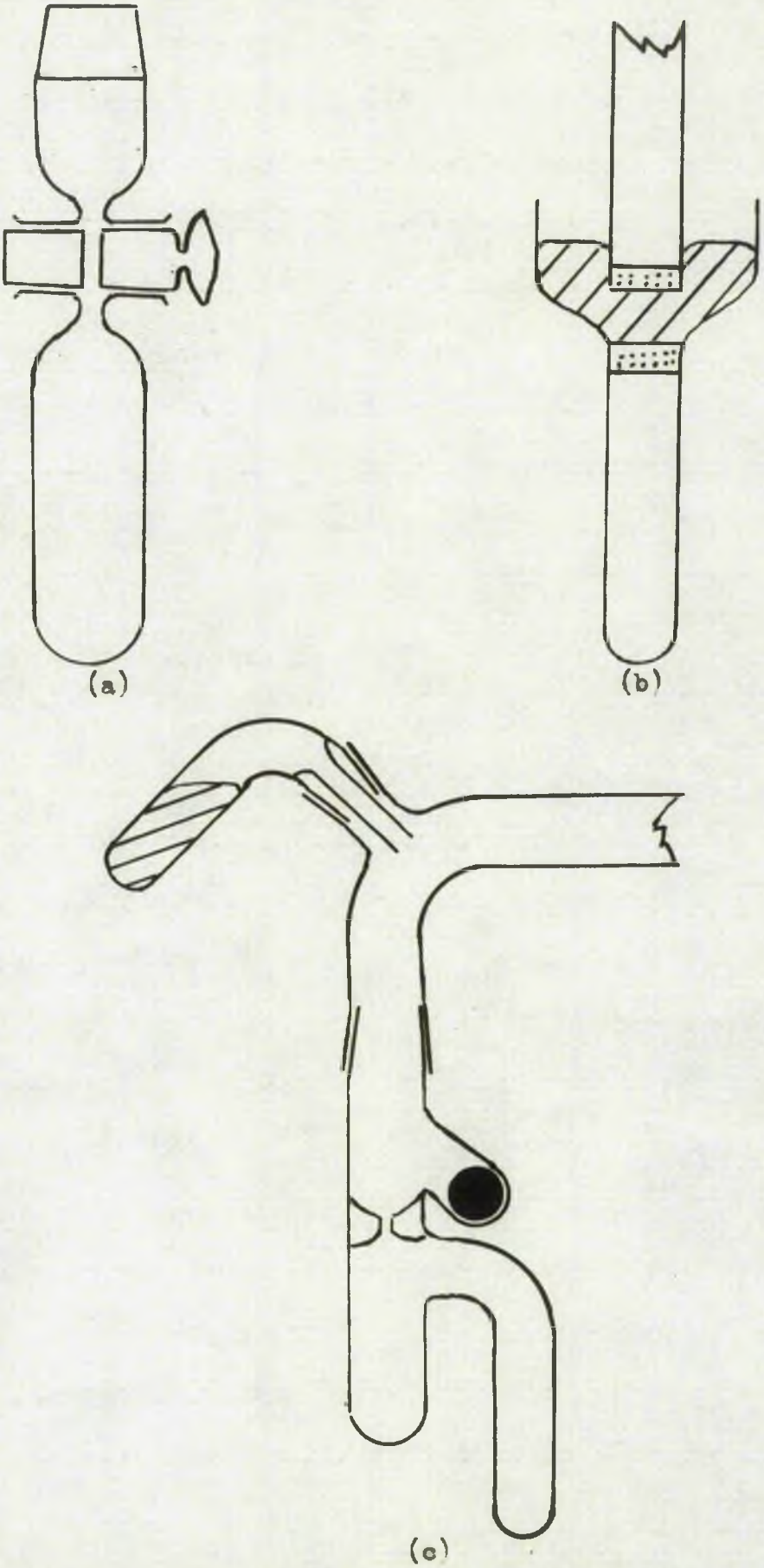


between components made it impossible to estimate composition by direct calibration. With so many variables present, accurate analysis could only be achieved by comparison with known mixtures. It was decided, therefore, to estimate the composition of the products sample roughly by inspection of its mass spectrum, synthesise a mixture of this composition, and compare the peak heights obtained for both samples. By this means, the composition of the calibration mixture could be adjusted to within 15% of the unknown, comparison of these giving accuracy to within 2%.

To synthesise a calibration mixture, a more sensitive form of burette than the 'Agla' syringe was required, since it was necessary to maintain low pressures in the sample handling system. A design by Gilmont (58) was modified to meet these requirements - Figure 11. A uniform piston of 1/16th. in. steel, actuated by a micrometer screw, displaced mercury in a 3/32 in. bore Pyrex capillary and this in turn ejected the liquid. A series of soft rubber gaskets and close fitting steel washers prevented any leakage of air into the piston chamber when the jet of the burette touched the evacuated sinter. One mm. travel of

Figure 12

Sample Holders.



the micrometer screw delivered 2.01×10^{-3} ml. to an accuracy of 1%. Two such burettes were constructed for styrene and toluene, and a third with a 1/32nd. in. piston, delivering $6.15 \cdot 10^{-3}$ ml./mm., for benzene. Calibration was accomplished by weighing on a microbalance the mercury displaced by the piston. Checks of reproducibility on the mass spectrometer indicated that the first 5 mm. travel of the piston of a newly filled burette gave inaccurate delivery, possibly due to some backlash at the gaskets. This portion was therefore rejected and the remaining 20 mm. used for calibration.

Sample Holders

Some system was required for the transportation of the small quantities of liquid products of a run from the flow apparatus to the mass spectrometer without evaporation losses or contamination by air, water vapour, or carbon dioxide.

A holder of the type shown in Figure 12a was tried, using a fluorocarbon lubricant on the solid key tap. This tap-grease was not successful, as it hardened quickly, 'freezing' the tap, and retained considerable quantities of the

products.

As many devices employing mercury sealed sintered discs are cited in the literature, e.g. (59), for the delivery of gaseous and liquid calibration samples, it was decided to investigate their possibilities for total transfer of the products. For the sinter, small plugs of fine grade carborundum were first tried, but these failed to seal into the pyrex holders. Metrosil 4F discs (1/4" diam. 1/16" thick) were obtained, and a small test system (Figure 12b) constructed. The region above the upper disc was attached to the vacuum line, and the discs pressed together. After 30 minutes pumping, several millimetres of air remained in the sample holder. The method was, therefore, of little use for quantitative delivery.

Ampoules which could be sealed on the flow apparatus and broken in vac. in the sample handling system were considered, but as in the calibration work, proved rather clumsy.

At this time, the technique of grinding spherical sockets to give mercury tight seals with steel balls had just been perfected, so a sample holder having this type of cut-off valve

was tried. It proved successful, and, being simple to assemble and operate, was adopted. The final design, developed after trials of the original, is illustrated in Figure 12c. Three such containers were made, and attached to side arms in traps Tr. 2.

Operation

On completing a run, the taps T3 and T4 were closed. Traps Tr.2 and the sample holders were evacuated through T5., with liquid-air round Tr.2. to retain the volatiles. When a good vacuum had been achieved, T5 was closed and the products transferred to the sample holder. The steel ball was then dropped into its socket with a magnet, and the L-shaped side tube turned through 180°, spilling mercury over the ball. Air could then be admitted to the apparatus, and the sample holder removed and stored until the mass spectrometer was available for analysis. It was then attached to the handling system at the sample inlet and evacuated, with liquid-air on the container (Figure 9). Tap T7 was closed, the cut-off lowered, the ball lifted into its pocket, with a magnet, and the sample transferred to the side arm of the manifold. After raising the cut-off,

Table 4

m/e	Run No.5	Styrene	Toluene	Benzene
104	0.78	100.0	-	-
103	0.24	48.1	-	-
102	0.043	8.70	-	-
93	0.19	-	5.90	-
92	2.01	-	64.5	-
91	3.45	3.07	100.0	-
90	0.19	0.28	4.86	-
89	0.19	2.23	4.53	-
79	0.47	3.46	0.14	8.90
78	1.47	46.9	1.51	100.0
77	0.47	24.0	1.37	26.7
76	0.07	5.59	0.41	7.56

the sample was expanded into the system and scanned.

Providing care was taken to ensure that the ball and its seat were free from grit, the sample could be stored in this way for weeks if necessary without loss. The minimum quantity of tap grease required to prevent leakage was used on all taps and joints in the path of the products to prevent loss by absorption.

Qualitative Assay

The products of Run No.5 were scanned over the mass range 110 - 70. Table 4 lists the peaks of appreciable magnitude obtained, with background deducted. All of these could be accounted for by toluene, benzene and styrene, the major contributions of which are also listed, referred, in each case, to a value of 100 for the largest peak. The effects of interference on peak heights made it impossible to sum the contributions exactly, but the fragments were all in good agreement with the parent peaks.

The absence of a peak at mass 106 confirmed the conclusion of [illegible].E. Miles that no ethylbenzene was formed during the reaction. Investigation of the masses 44 and 30, the largest peaks of

propane and ethane indicated the complete absence of these. A scan of 44 - 70 also displayed nothing which could not be accounted for. The conclusion was, therefore, that the trap Tr.2. contained toluene, benzene and styrene only.

Quantitative Analysis

Routine analysis took the following form. A suitable trap current was selected, depending on the state and age of the filament. A series of measured samples of toluene was injected, followed in each case by a nitrogen sample, until the instrument gave consistent results. The manifold was then evacuated, the background for the masses 104, 91 and 78 noted, and the products admitted. These were thoroughly mixed and the peak heights for the above masses noted. Immediately afterwards, the products were condensed into the side tube, the 28 background recorded, a 2 mm. sample of nitrogen admitted, and its peak height recorded. The latter operations were performed as soon after noting the hydrocarbon peaks as was possible. The manifold could then be pumped out in preparation for the next sample.

After three samples from the run had been scanned, their compositions were estimated and a

calibration sample prepared and scanned. The overall time for this work was generally between 3½ - 4 hours, each sample and calibration taking 30 minutes, the rest of the time being devoted to conditioning the filament and ionisation chamber with toluene samples.

(c) The Gases

Although no increase in carrier gas pressures could be detected during an experiment, it was decided to analyse the gaseous materials at the end of one of the runs. For this a Toepler pump and a small reservoir were constructed and attached between tap T1 and the circulating pump. The gases were collected and the reservoir attached to the mass spectrometer.

A mass spectrometer scan indicated the presence of a trace of hydrogen, no methane, and no ethane. The hydrogen concentration was so small as to be unimportant in the reaction sequence, though its production did in fact take place.

Conclusions Regarding Analytical Methods

The mixture of solids consisted of unreacted dibenzyl, stilbene, and a small quantity of unidentified material, possibly dimethyldiphenyls. The two main components could be

quickly and accurately determined by ultra-violet spectrophotometry to within ± 1%.

The liquid products were styrene, toluene, and benzene, the assay of which by mass spectrometry could, under suitable conditions, achieve an accuracy of ± 1% for styrene and toluene, ± 2-3% for benzene. No other components could be detected.

The gaseous residues revealed a small proportion of hydrogen which was only just detectable by mass spectrometry.

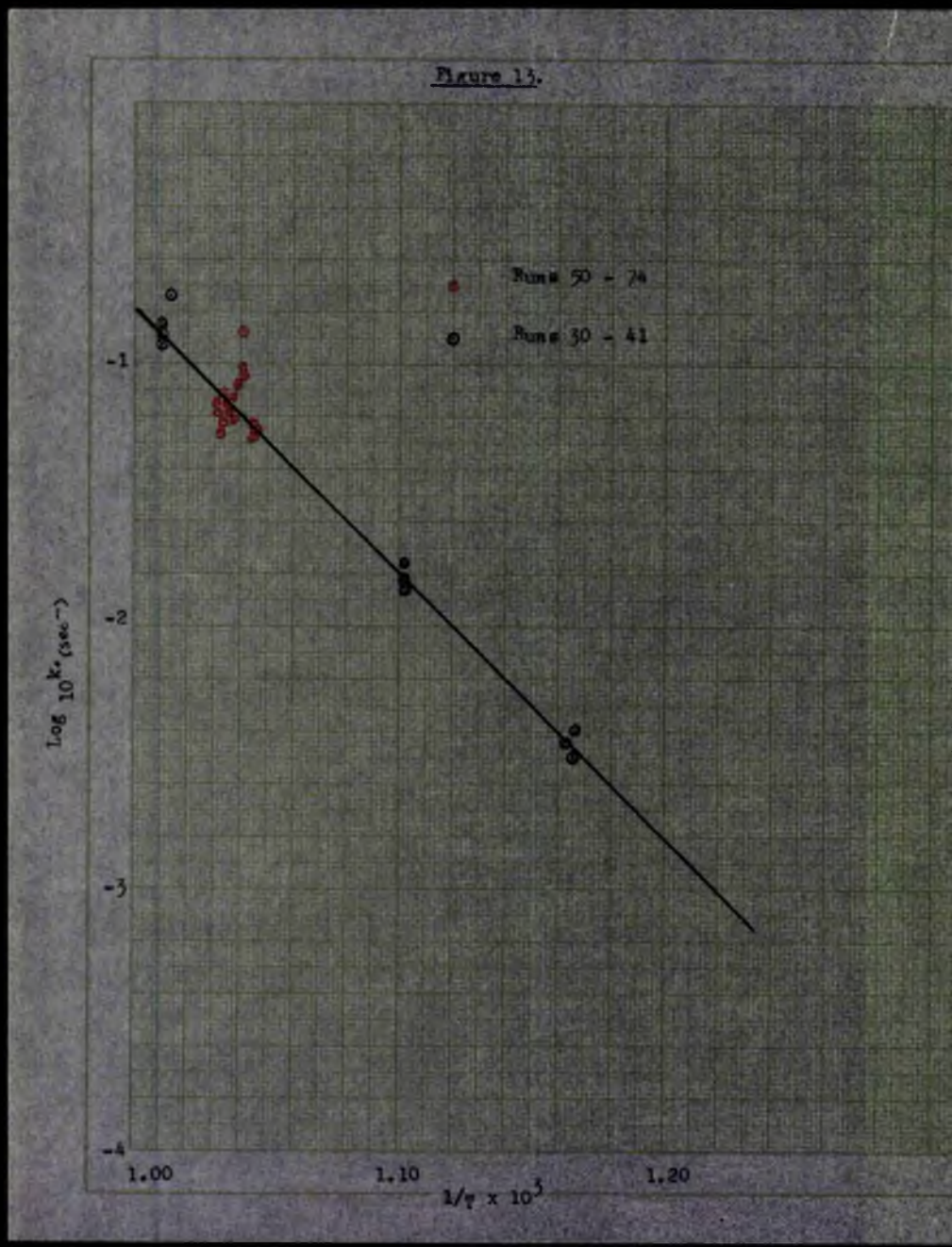
Experimental Results

Runs No.1-20 were used for qualitative investigations and development of techniques. As the degree of accuracy of analysis was not sufficient for quantitative studies, their results were not recorded.

The first objective was the corroboration of the findings of S.E. Miles, and for this the effect of temperature variation on the rate of formation of products was investigated. - Runs No. 30-47. Following Miles, it was assumed

(a) that the slowest step in the reaction sequence was the rupture of the central carbon - carbon bond to give benzyl radicals;

Figure 13.



(b) that all these radicals formed toluene, and took no part in side or back reactions;

(c) that the decomposition followed a first order law.

On these assumptions a plot of the log. of the first order rate constant against reciprocal temperature (^{o}K) was drawn - Figure 13. This gave a straight line plot which could be represented by $k(sec^{-1}) = 10^{9.15} exp.(48.k.cal./RT)$. To confirm assumption (c), the partial pressures of dibenzyl and carrier gas were varied - Runs No.50-74 - and their log.k / 1/T coordinates plotted on the same graph. They showed considerable scatter about the line, although there appeared to be no systematic deviation with pressure.

It would have been more satisfactory to have plotted the velocity constant against the partial pressure of dibenzyl and carrier gas separately, but the method of pick-up by saturator made it impossible to vary one condition without altering others. For instance, if the partial pressure of carrier gas was changed appreciably, the rate of pick-up of dibenzyl changed also, as did the rate of flow.

Comparison with S.E. Miles

The dependence $k(sec^{-1}) = 10^{9.3}exp.(48.0k.-cal./RT)$. found by Miles was in excellent agreement with the present work. It appeared, therefore, that a temperature independent factor of 10^9 was justified if the assumptions mentioned above were correct. These seemed to be upheld by the runs in which partial pressures were varied, as the scatter there appeared to be due to experimental error rather than deviation from first order behaviour.

The nature of the products obtained agreed in the main with the previous work, the presence of a small quantity of material absorbing in the far U/V, and a trace of hydrogen being the only differences.

Quantitatively, however, the correspondence was not so good. Toluene was undoubtedly in greatest concentration, but whereas Miles found benzene and styrene to be equal, in the present case the ratio styrene/benzene varied from 2.6 at 716°C to 1.7 at 585°C. Similarly toluene/styrene and toluene/stilbene ratios were not constant - see Table 7). A more thorough examination of this is to be found in the Discussion Section.

The Fluorene Experiments

The close correspondence existing between the observed activation energy obtained above and the value for the bond energy obtained by calculation from heats of formation data seemed to confirm the validity of the assumptions, yet the anomalous temperature independent factor indicated that the observed reaction rate was slower than would be expected for a first order mechanism by a factor of 10^4. Hence, either the bond energy parallelism was purely coincidental, and the reaction mechanism other than that postulated, or there was, for some reason, a very large 'steric factor' involved.

It was decided first to investigate the reaction mechanism. Possible alternatives were:

1. A strong back reaction.

$$2Ph.CH_2 \longrightarrow Ph.CH_2.CH_2.Ph.$$

2. A reaction mechanism in which free radicals were not involved, or in which they formed only a part of the sequence.

3. The rate determining step was not the initial split to benzyl radicals, but some other reaction in the chain. Suggestion No.1 would be an example of this.

In an attempt to illustrate the free radical nature

of the reaction, Niles had investigated the decomposition of benzyl iodide and α-azo toluene alone, and benzyl iodide in the presence of dibenzyl. Working between 600-700°C, temperatures at which total decomposition of these compounds occurs, the liquid products from the pyrolysis of benzyl iodide and α-azo toluene closely resembled those from dibenzyl, the toluene formed accounting for about 26% of the benzyl radicals produced. In the presence of dibenzyl, the toluene concentration from benzyl iodide increased several fold, and approached the concentration of benzyl radicals admitted, apparently indicating that benzyl radicals attack dibenzyl to form toluene. It would have been more informative, however, if the work had been done at lower temperatures where decomposition of the dibenzyl did not occur. Moreover, it has recently been shown (45) that at the high temperatures used, iodine atoms are capable of attacking hydrocarbons.

It would have been more satisfactory if some compound had been added which was capable of combining with the radicals before they had time to react with the parent compound. The benzyl radical is, however, relatively stable, and has been shown to be unaffected by the presence of nitric oxide and oxygen (60). Consequently the normal radical acceptors are useless.

Recent work on fluorene by McCrae (52) had suggested that this compound might be suitable as a radical catcher. His work has shown that:

1. The activation energy of the methylenic C-H bond is 68.5k.cal./mole. This is 9 k.cal. less than the methylenic bond in toluene, and hence fluorene would be very effective as a hydrogen donor for free radicals.
2. The radical formed when a hydrogen atom is lost, is removed by dimerisation, and takes no part in side reactions. Thus it would not interfere in any other reaction taking place concurrently.
3. Measurable decomposition does not occur at temperatures high enough to produce a 1% decomposition of dibenzyl, and so no interference is likely.

One would expect the methylenic C-H bond in dibenzyl to be appreciably stronger than that of fluorene, and hence, if the mechanism postulated by Miles is correct, the presence of fluorene in the reaction chamber should reduce the formation of the radical $Ph.CH.CH_2.Ph.$ and consequently the secondary products stilbene, styrene, and benzene. If no back reaction exists, the toluene formed would be independent of the concentration of fluorene. If, however, a back reaction

is appreciable the production of toluene would increase with increased partial pressure of fluorene, the degree of increase falling off to zero as "saturation" conditions are approached. Should the reaction proceed by some mechanism not involving free radicals, the addition of fluorene would have no influence on the products.

Method

A system was required whereby a fixed concentration of dibenzyl and a variable concentration of fluorene could be admitted into the gas stream together. The coupling of two saturator units in parallel was undesirable owing to the difficulty of maintaining a constant supply of one while varying the other. Moreover, the high extinction coefficient of fluorene (1.35×10^4 at 268mμ.) made it impossible to determine the concentration of dibenzyl in admixture. It was desirable, therefore, to have some system of injection into the gas stream which could be predetermined, and would remain constant despite alterations in total pressure.

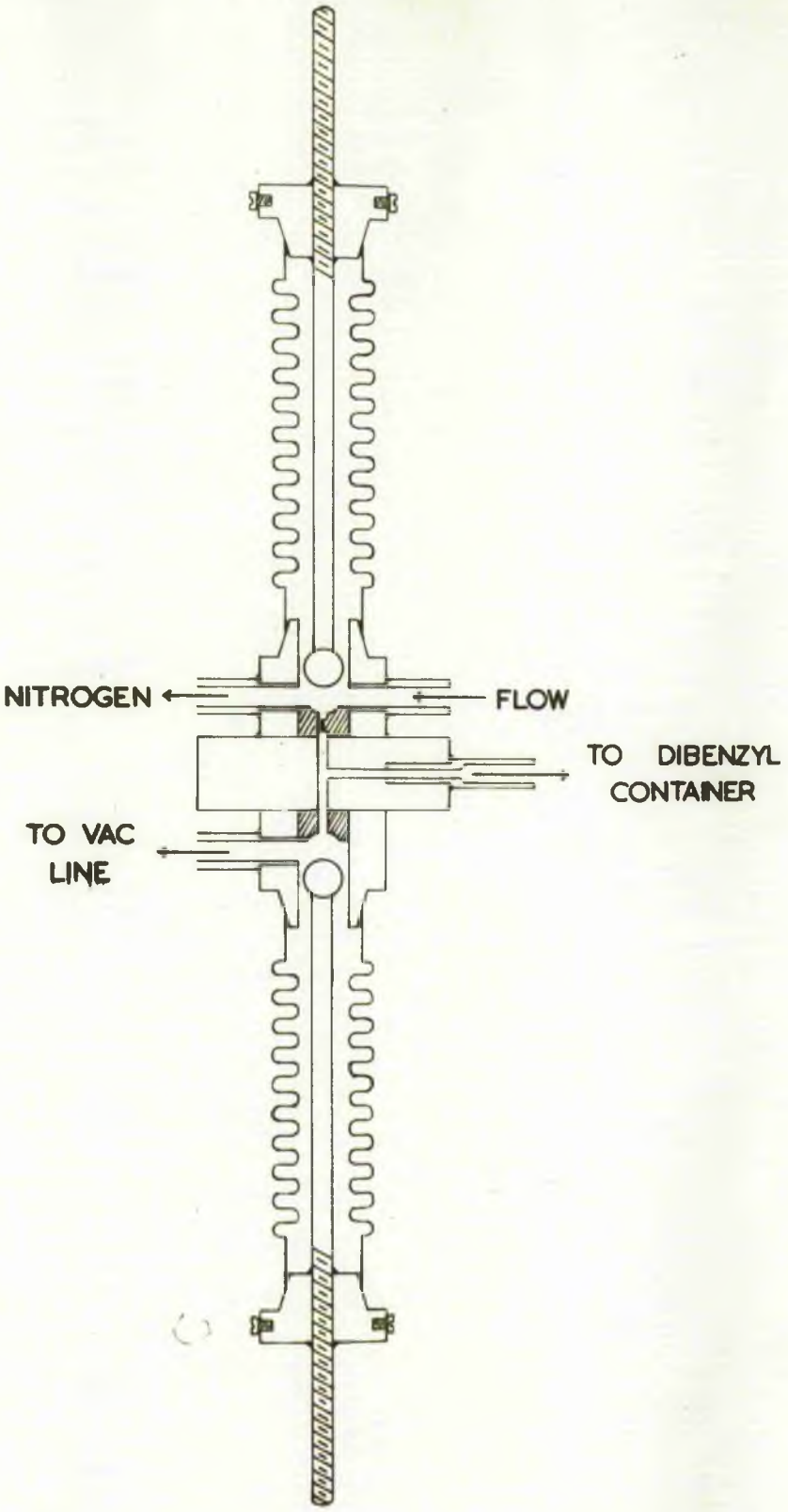
Injection Units

The essentials of such a system were:

(a) a reservoir which could be heated to a temperature sufficient to produce a high vapour pressure of

Figure 14

Injection Units



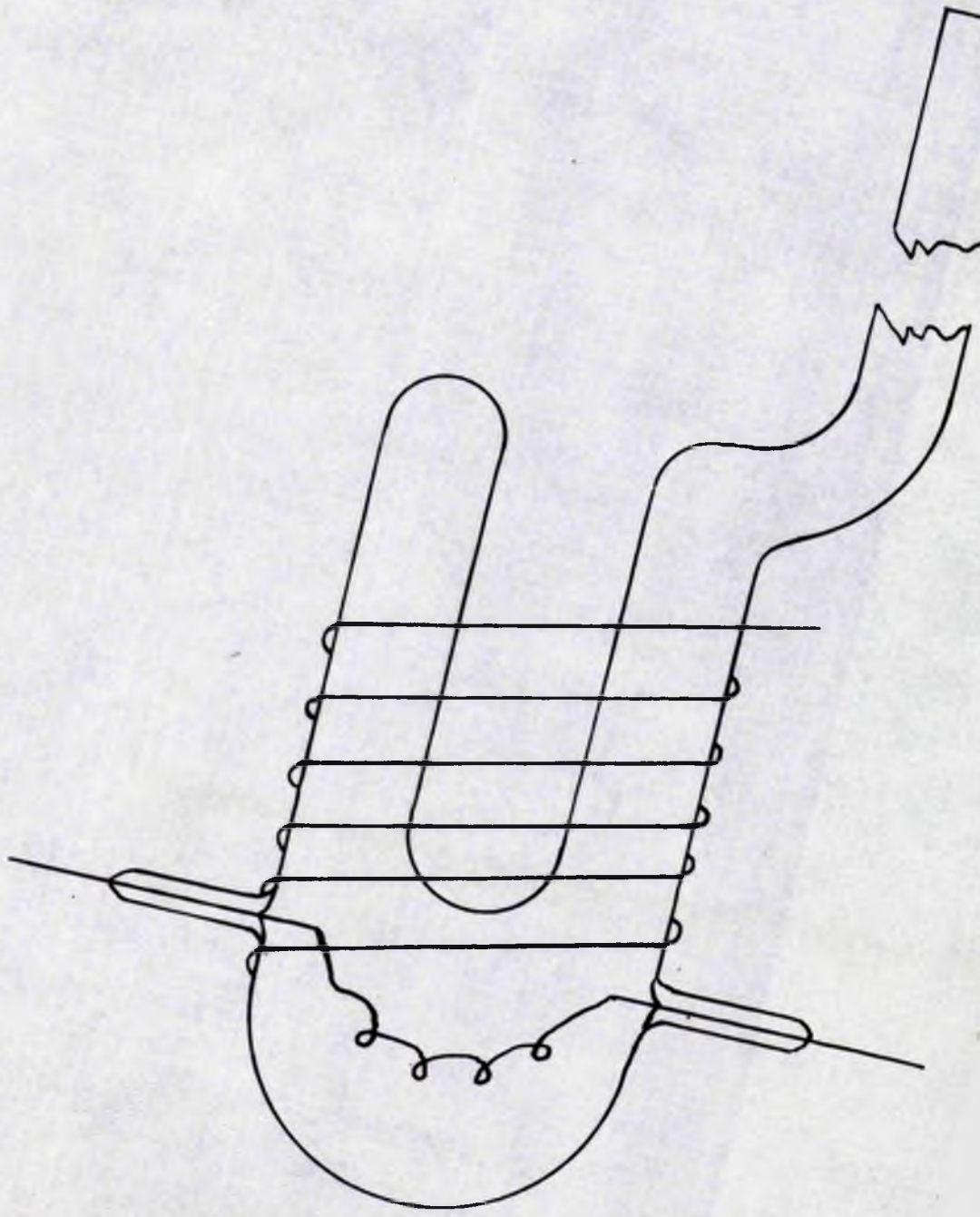
reactant; and

(b) a jet through which the vapour could be streamed into the circulating stream.

Provided that the pressure on the reservoir side of the jet was kept above 20mm., a change of 1mm. on the low pressure side would not have an appreciable effect on the rate of flow through the orifice.

As temperatures of 100°C - 150°C were required to prevent condensation on the walls, glass taps could not be used as cut-offs. A pair of all-metal valves were therefore constructed, employing stainless-steel bellows which allowed a 1/4" compression. Details of these are shown in Figure 14. The valves themselves consisted of 5/8" rustless steel balls seated in shaped copper blocks, one of which carried a 0.0007" diameter jet, the other having a wide aperture for evacuation of the reservoir. These were mounted on either side of a 1½" diameter mild steel disc which also carried the reservoir. Side arms in the injection valve directed the nitrogen stream over the jet, thus ensuring no dead space in which the reactant vapour could collect. The reservoir itself was a pyrex tube coupled to the system by a graded metal-to-glass seal, and was maintained at a constant temperature by surrounding it with a specially designed bath - Figure 15 - in which a pure

Figure 15
Constant Temperature Bath



liquid was refluxed gently. As slight variations in the temperature of this bath could cause serious alterations in the rate of injection, carefully purified liquids were used, and the heat supplied by a spiral of resistance wire inside the vessel to prevent superheating. By changing the bath fluid, a range of partial pressures could be obtained from 0.08mm. upwards.

Calibration

The unit was inserted between the existing saturator and the furnace by standard tapered joints sealed with "Polythene" wax. Blank runs were performed using dibenzyl alone at a furnace temperature of 300°C. The valve was opened for periods of 15 minutes, and the dibenzyl collected and analysed by U/V spectrophotometry.

The results from six runs proved to be very inconsistent. Investigation showed that dibenzyl could be collected from the gas stream 10 - 15 minutes after shutting down. That this was not due to faulty seating of the valve was proved by cooling the reservoir in liquid-air immediately after closing the valve. No cool spots, on which dibenzyl could condense, were to be found on the furnace inlet and outlet lines. The trouble was eventually traced to the "Polythene" joints

by which the metal injection unit and the silica furnace were coupled to the pyrex flow system. These were maintained a few degrees below the melting point of the wax, and, under such conditions, polythene proved capable of absorbing more than half of the dibenzyl injected, releasing it gradually as the supply was cut off. The joints were replaced by metal/pyrex and silica/pyrex graded seals, the calibrations repeated, and reproducibility found to be consistent to 2 - 3%, an accuracy which was ample for the intended work.

For the first few mixed runs, the existing saturator was used for the fluorene pick-up, but after the injection system had proved its worth, a second unit was built and installed in its place.

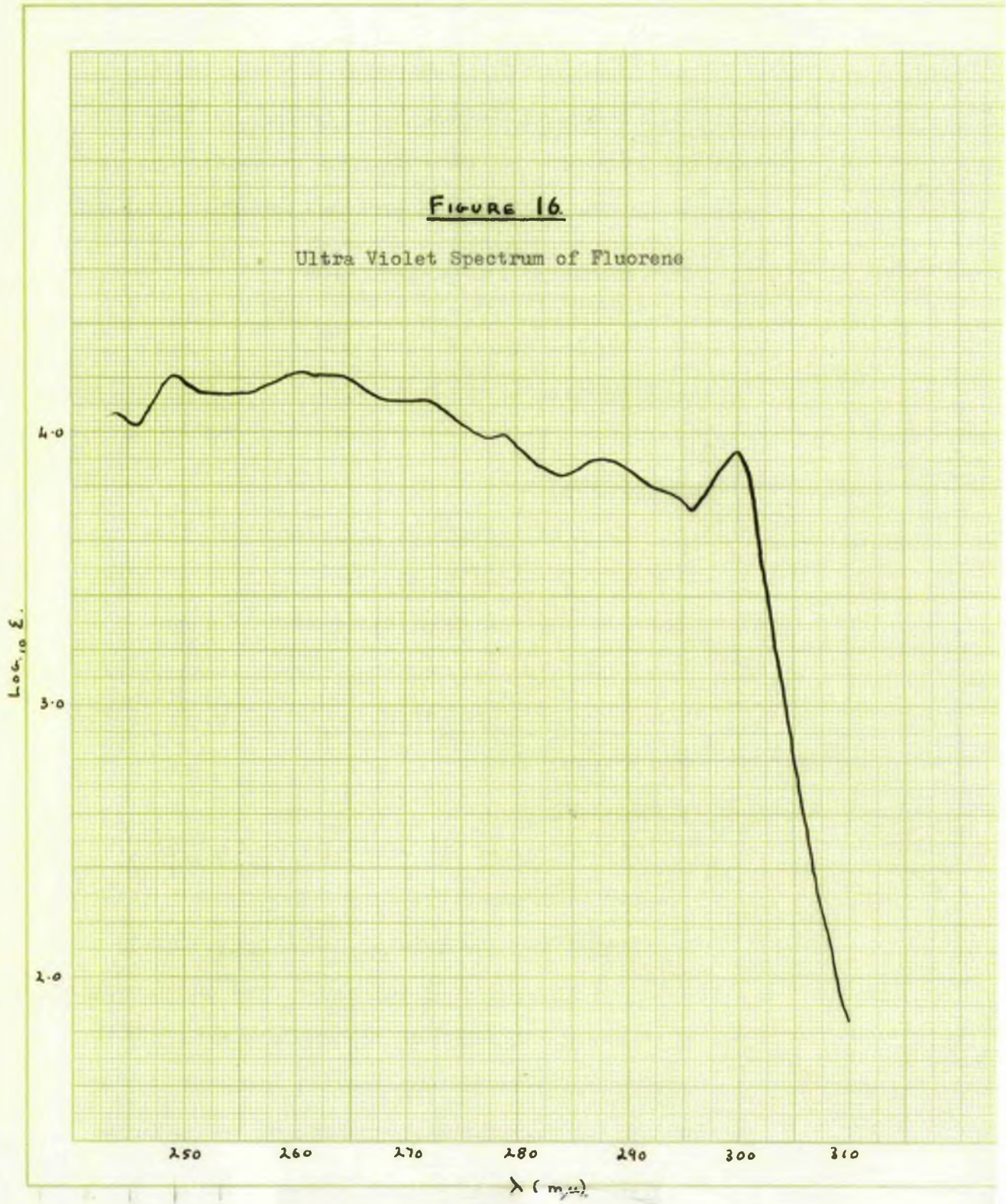
Operation and Analysis

When the carrier gas flow had reached equilibrium, the fluorene valve was opened and allowed to stream alone for 30 seconds. Dibenzyl was then admitted for a measured time, and the valve shut down. After a further 30 seconds, the fluorene unit was also closed.

The products were collected as before, fluorene condensing with dibenzyl and stilbene in trap Tr.1. Difluorenyl, being relatively involatile, condensed in the furnace outlet and was removed later by heating with a gas flame.

FIGURE 16.

Ultra Violet Spectrum of Fluorene



As Figure 16 shows, fluorene does not absorb light of wavelength greater than 310mμ. It was possible therefore to determine the concentration of stilbene in admixture since stilbene absorbs strongly at 320mμ. The contribution of this and the predetermined concentration of dibenzyl could then be deducted from the absorption at shorter wavelengths, and the proportion of fluorene determined to within 2%.

Results

(a) Qualitative

The high extinction coefficient of fluorene made it impossible to detect the presence in the solids of any resultant other than stilbene.

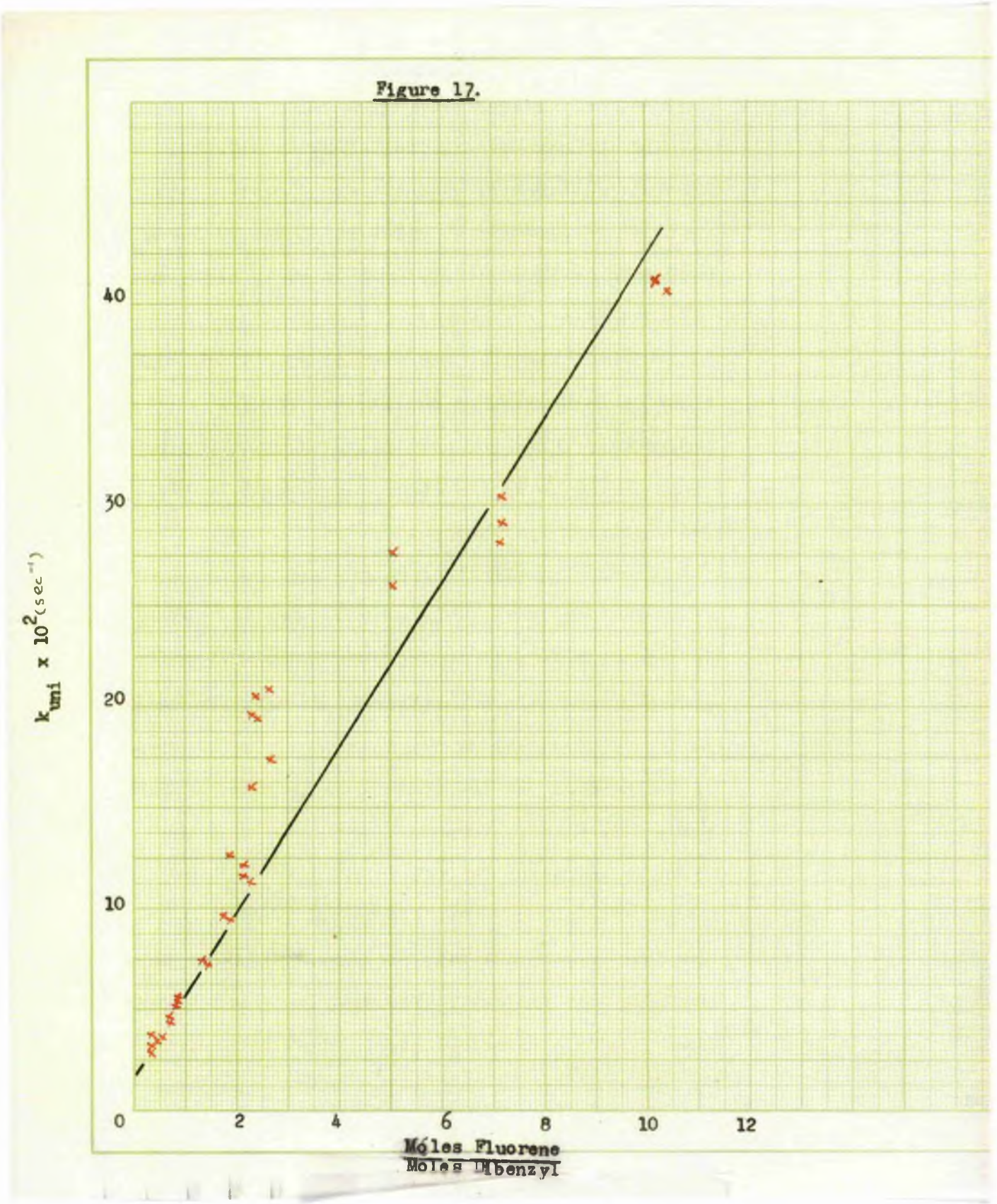
A mass spectrum of the liquids proved that these were identical with the products obtained from dibenzyl alone.

(b) Quantitative

Comparison of the products obtained from dibenzyl with those from a mixture with fluorene showed that the presence of the latter greatly increased the yield of toluene. The concentrations of stilbene, styrene and benzene remained fairly constant, though the accuracy of analysis of the latter was considerably impaired by the presence of such a large excess of toluene.

A plot of the calculated first order rate

Figure 17.


40
30
20
10
0
2
4
6
8
10
12
$k_{uni} \times 10^2 (sec^{-1})$
Moles Fluorene
Moles Dibenzyl

constant for toluene production against the partial pressure of fluorene added at constant partial pressures of dibenzyl and nitrogen, and constant temperature is shown in Figure 17 for a variation in fluorene pressure up to 10 times the concentration of dibenzyl. Although there is considerable scatter, the plot rises steeply, and shows no indication of falling off at high pressures. Thus the rate of production of toluene would appear to be directly proportional to the concentration of fluorene.

As the reaction temperature was too low for appreciable decomposition of fluorene, the increased toluene production can only be accounted for by assuming a high concentration of benzyl radicals removing methylenic hydrogen atoms. The presence of difluorenyl and the absence of hydrogen confirm this. It appears certain, therefore, that one stage in the decomposition is the formation of benzyl radicals by splitting of the central C-C bond, and, as the quantity of toluene produced does not influence the other products, it is not likely that this is a secondary step. Furthermore, the 20 fold increase in toluene production indicates that the rate of formation of benzyl radicals is

very much greater than was suspected and hence a vigorous back reaction must occur. Miles' basic assumption that the formation of benzyl radicals is the rate determining step is not, therefore, acceptable.

The straight line dependence of toluene production on fluorene concentration indicates a constancy of benzyl radical concentration even when 10% of the injected dibenzyl is lost as products. Assuming first order conditions for the decomposition to benzyl radicals, and a temperature independent factor of 10^{13}, the rate of formation of radicals would be greater than the rate of formation of toluene by a factor of roughly 10^{4}. Hence, either there is complete decomposition of dibenzyl in the furnace, dimerisation and secondary reactions occurring only in the cooler outlet, or a very fast back reaction exists in the furnace, so that an equilibrium state results, maintaining a small but constant concentration of benzyl radicals. The latter case could be represented by the equation:-

$$Ph.CH_2.CH_2.Ph \xrightleftharpoons{K} 2Ph.CH_2.$$

Under such circumstances, the rate of formation of toluene cannot have first order dependence, and any values calculated on this assumption must be

valueless. The fluorene experiments demonstrated that one path at least for toluene formation is the abstraction, by benzyl radicals, of methylenic hydrogen, as postulated by Miles. From the high concentrations of toluene obtained in the presence of fluorene, and the similarity of the methylenic C-H bonds in fluorene and dibenzyl, it is likely that the bulk of the toluene is produced in this way. Thus the dependence of toluene formation on radical concentration can be estimated from:-

$$Ph.CH_2\cdot + Ph.CH_2.CH_2.Ph \xrightarrow{k_a} Ph.CH_3 + Ph.CH.CH_2.Ph$$

$$\frac{d}{dt}(Ph.CH_3) = k_a(Ph.CH_2\cdot)(Ph.CH_2.CH_2.Ph)$$

If equilibrium conditions exist, then the concentration of benzyl radicals in the furnace zone can be calculated as a function of dibenzyl

$$K = \frac{(Ph.CH_2\cdot)^2}{(Ph.CH_2.CH_2.Ph)}$$

$$\therefore (Ph.CH_2\cdot) = K^{0.5}(Ph.CH_2.CH_2.Ph)^{0.5}$$

(if the dissociation is small)

Substituting in the equation for the rate of formation of toluene

$$\therefore \frac{d}{dt}(Ph.CH_3\cdot) = k_a.K^{0.5}(Ph.CH_2.CH_2.Ph)^{1.5}$$

$$= k_{1.5}(\text{Dibenzyl})^{1.5}$$

Thus, if the assumption of an equilibrium

state is correct, the rate of formation of toluene should display a 1.5 order dependence on the concentration of dibenzyl, i.e. a plot of partial pressure of dibenzyl against rate constant calculated from a 1.5 order equation should give a horizontal straight line.

To test this hypothesis, further work was carried out on dibenzyl alone using constant temperature conditions.

Re-investigation of Dibenzyl Alone

With an injection unit replacing the saturator, it was now possible to investigate more accurately the effect of varying partial pressure. As, however, it was obvious that first order conditions did not prevail, it was necessary to eliminate as many of the variables as possible. Partial pressure of nitrogen, and consequently contact time, could only be roughly adjusted with previous arrangements. A manostat - Figure 18 - was therefore constructed and installed between the nitrogen reservoirs and the circulating system. A fixed quantity of mercury in the unit caused it to cut off at 120mm, and the volume of gas trapped at this pressure was adjusted by selecting the size of the flask attached to the side arm to the nitrogen supply. Fine adjustment could be accomplished by partially filling the

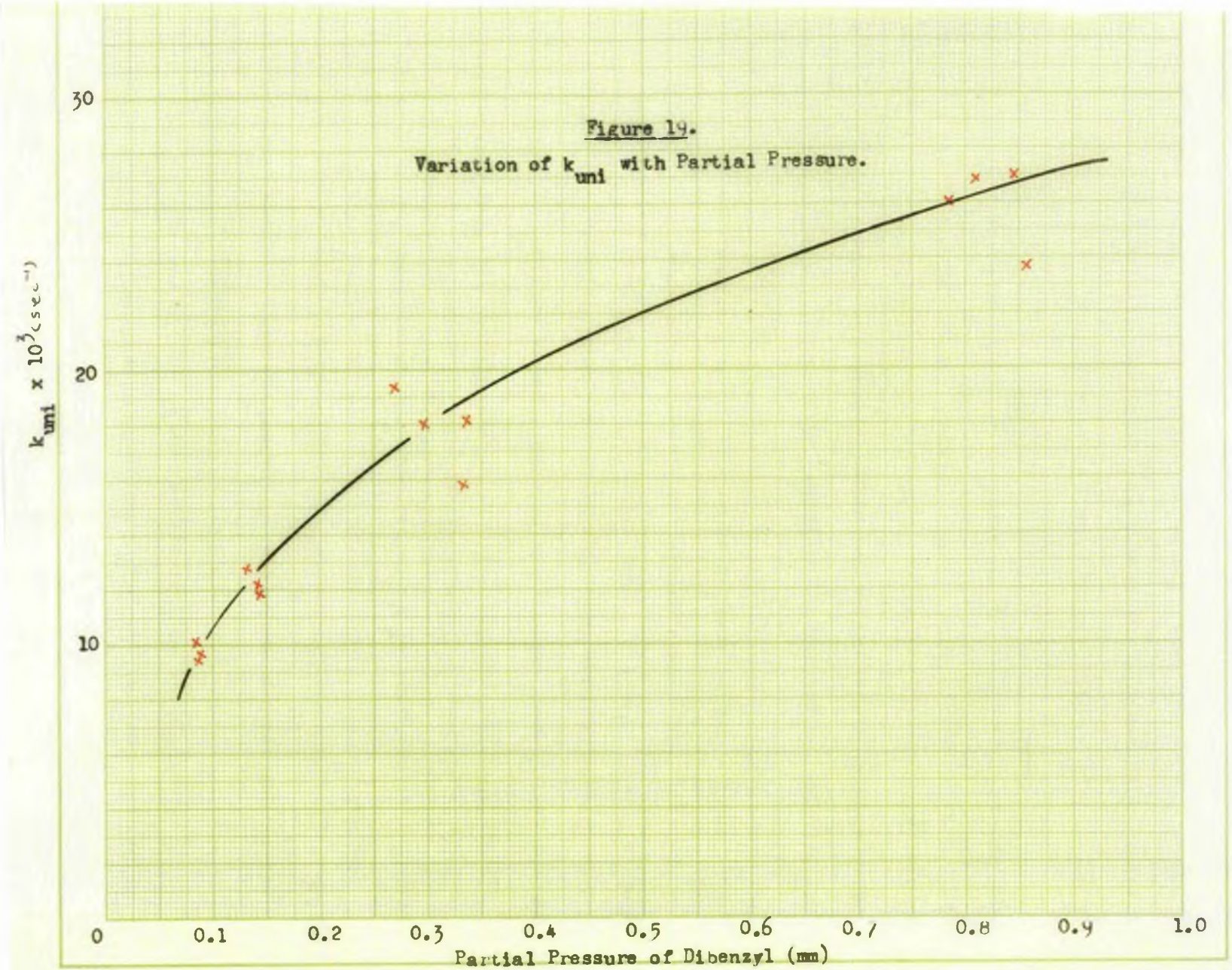


Figure 19.

Variation of k_{uni} with Partial Pressure.

flask with mercury. As a further refinement, the flask was immersed in a bath of ice water to reduce the effect of variations in room temperature.

Procedure

The apparatus was evacuated and the tap to the circulating system closed. Nitrogen was then admitted to the manostat from the reservoir, depressing the mercury on the expansion side of the U-tube. Excess nitrogen was pumped out through the sinter until a pressure of 120mm. was attained, at which point the rising mercury cut off the pumping line. The tap to the circulating system was then opened, and the gas expanded into the apparatus. A 100ml. flask together with the volume of the manostat was sufficient to supply a static pressure of 4mm. to the system.

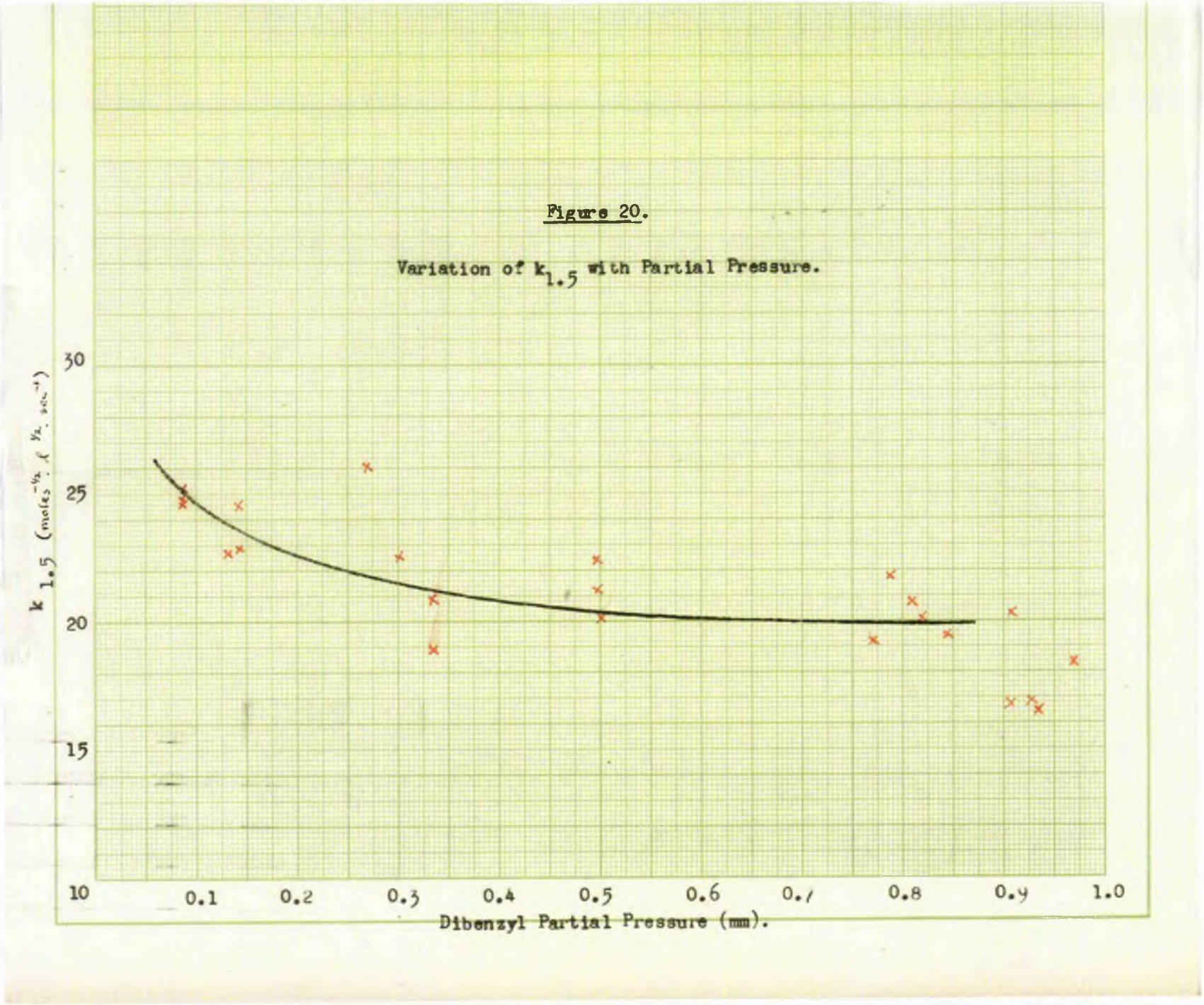
Results

The rate of formation of toluene was investigated over the dibenzyl pressure range 0.08 - 1.0 mm. under conditions of constant temperature and nitrogen pressure. Plots of k_{uni} and $k_{1.5}$ calculated on toluene production, against partial pressure of dibenzyl, are illustrated in Figures 19 and 20 respectively.

The first order plot gave a sharply rising curve, the rate constant increasing by 250% over the investigated pressure range. The 1.5 order graph did not give a

Figure 20.

Variation of $k_{1.5}$ with Partial Pressure.



constant value for $k_{1.5}$, but the variation with pressure was very much less - roughly 50%. An overall reaction order of 1.5 appeared therefore to be a closer approximation to the true state than was the first order scheme employed previously.

Returning to the results of Runs 30 - 41, rate constants were calculated on a 1.5 order basis, and plotted as before - Figure 21 - giving a value of 47.6 k.cal./mole for the overall activation energy of the reaction.

As the partial pressure of dibenzyl appreciably influenced the values of the rate constant at one temperature, a series of experiments was performed to determine how this varied with temperature. A lower partial pressure of dibenzyl was maintained, and the temperature varied over the same range. The inverse temperature plot of these results showed considerable divergence from the earlier work, and gave an activation energy of 38.2 k.cal./mole.

From evidence put forward in the discussion section of this thesis, it can be seen that a more useful value for the activation energy of the reaction would have been obtained had a higher partial pressure been used, as the reaction approximated more closely to true 1.5 order at 0.5 mm. or greater. Unfortunately this did

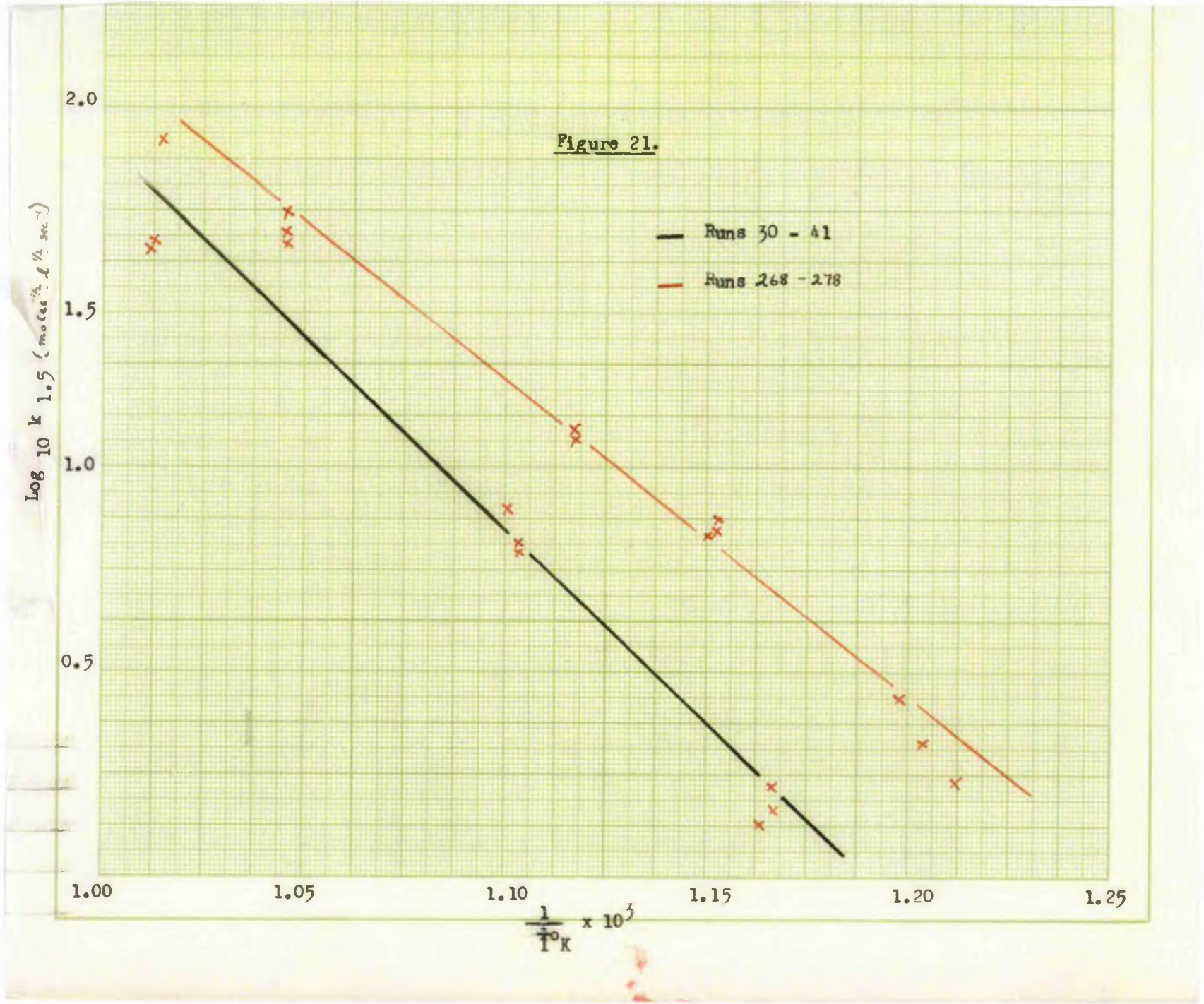


Figure 21.
Runs 30 - 41
Runs 268 - 278
Log 10 k 1.5 (moles^½ l^½ sec^-1)
2.0
1.5
1.0
0.5
1.00
1.05
1.10
1.15
1.20
1.25
1/T°K x 10^3

not become apparent until more data had been collected, and by then there was insufficient time left to carry out such experiments.

Further Studies

After the work on pyrolysis discussed above, two possible lines of investigation were open.

(1) The direct determination of the activation energy for the initial step

$$Ph.CH_2.CH_2.Ph \longrightarrow 2Ph.CH_2.$$

which would give a value for $D(Ph.CH_2-CH_2.Ph)$

(2) The investigation of the reaction

$$Ph.CH_2. + Ph.CH_2.CH_2.Ph \xrightarrow{Ea} Ph.CH_3 + Ph.CH.CH_2.Ph$$

in the hope that this would throw some light on the reaction mechanism, and give a value for the activation energy Ea.

Case (1) was the first to be examined, as a direct determination was more desirable and did not involve the independent production of free radicals. If equal quantities of dibenzyl and a:a',b:b', tetradeuterodibenzyl are pyrolysed together by the flow technique, then, if a fast back reaction exists, one of the resultants should be a:a' dideuterodibenzyl.

i.e. $Ph.CH_2.CH_2.Ph \longrightarrow 2Ph.CH_2.$

$Ph.CD_2.CD_2.Ph \longrightarrow 2Ph.CD_2.$

$Ph.CH_2. + Ph.CH_2. \longrightarrow Ph.CH_2.CH_2.Ph$ (1)

$Ph.CD_2. + Ph.CH_2. \longrightarrow Ph.CH_2.CD_2.Ph$ (2)

$Ph.CD_2. + Ph.CD_2. \longrightarrow Ph.CD_2.CD_2.Ph$ (3)

It is obvious that products (1), (2), and (3) should be formed in equal amounts under these conditions. Thus, by determining the concentration of this substance in the mixture of products and starting material, the percentage initial decomposition could be measured.

For an accurate determination of the rate constant, this method requires a mass spectrometer of high resolution, (1 in 200 at least) and an inlet system which can be heated to a temperature of one hundred degrees or more to prevent condensation of dibenzyl vapour. As the resolution of the existing mass spectrometer was at best 1 in 100, and as the high resolution instrument under construction had not been completed at this stage of the work, it was decided to postpone investigations along these lines until the high resolution instrument was in operation, and to concentrate on the second approach during the interim period.

Case 2

If some method can be found for the production of

benzyl radicals which is independent of the temperature of the reaction vessel, then the temperature dependence of toluene production by the attack of these radicals on dibenzyl can be determined, and hence the energy of activation Ea for the radical-molecule reaction. The investigations must of course be carried out over a temperature range which produces a negligible concentration of benzyl radicals by thermal dissociation of dibenzyl, i.e. below 400°C.

A constant quantity of benzyl radicals can be obtained by the thermal decomposition of compounds of the type $Ph.CH_2.X$ where the C-X bond is so weak that total decomposition results at the furnace temperatures and contact times used. Compounds in this class are benzyl iodide, mercury dibenzyl, and w:w' diazotoluene, all of which are readily decomposed to form benzyl radicals. Benzyl iodide and azo toluene were both used by Miles for this purpose (see page 78). However, several obvious drawbacks must be noted.

(a) Although the total quantity of radicals formed in the reaction vessel may be independent of temperature, within the above-mentioned limits, their distribution along the vessel would depend on the rate of decomposition, and hence on the temperature. Thus the steady state concentration

of radicals at any fixed point in the vessel would vary with the necessary variations in furnace temperature.

(b) The unstable nature of these compounds would prevent the use of injection units for their introduction into the gas stream, as a high pressure could not be maintained in the sample reservoir without some decomposition. Hence the less satisfactory saturator system would have to be employed.

(c) Benzyl iodide would not be a satisfactory source of radicals, as it has been shown by Cundall (45) that iodine atoms are capable of attacking hydrocarbons, and so undesirable side reactions would result.

For these reasons pyrolysis was considered an unsatisfactory method for benzyl radical production, and another approach was sought.

The parallelism of the dibenzyl reaction and that between bromine and hydrogen (27)(28) suggested the possibility of using a photochemical technique for the initial dissociation of dibenzyl. Bodenstein's investigations of the thermal reaction between bromine and hydrogen (27) indicated that the primary process was the formation of an equilibrium concentration of

bromine atoms.

$$Br_2 \longrightarrow 2Br.$$

followed by the secondary reactions,

$$Br. + H_2 \longrightarrow HBr + H.$$

$$H. + Br_2 \longrightarrow HBr + Br.$$

Similarly, the work which has been discussed in this chapter suggests that the significant processes are:

$$Ph.CH_2.CH_2.Ph \rightleftharpoons 2Ph.CH_2.$$

$$Ph.CH_2. + Ph.CH_2.CH_2Ph \longrightarrow Ph.CH_3 + Ph.CH.CH_2.Ph$$

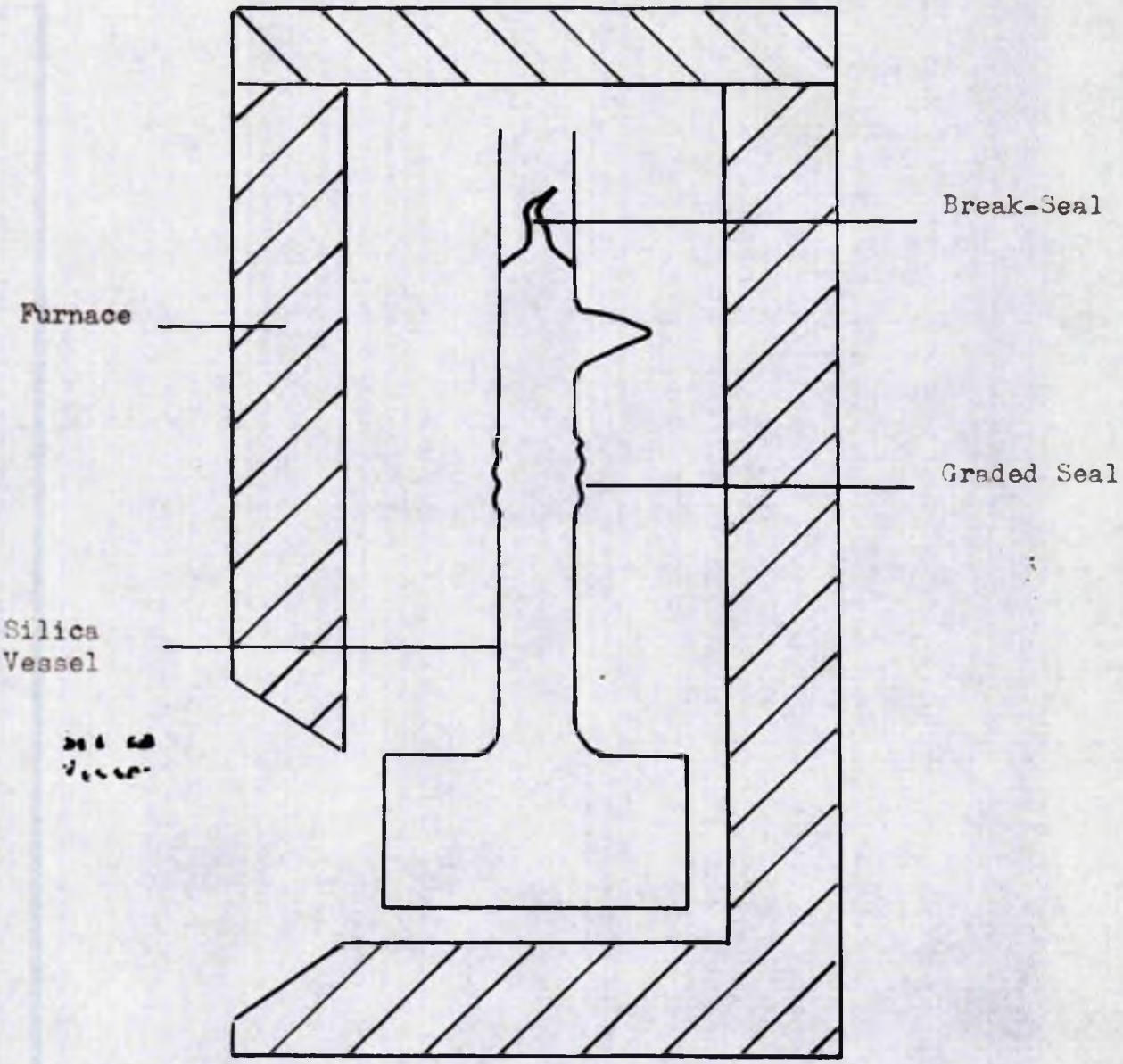
Little is known of the photodecomposition of such complex molecules as dibenzyl, but the exceptional stability of the benzyl radical and the exceedingly weak central C-C bond of dibenzyl were considered to be some small justification for further investigation. If benzyl radicals could be produced by this method, it might then be possible to determine the temperature dependence of subsequent reactions.

Even if benzyl radicals could be produced photochemically, it was realised that further complications might arise. Although the dissociation energy of the central C-C bond should have a value between 45 k.cal./mole (as calculated from Szwarc's data on toluene) and 69 k.cal./mole (from Van Artsdalen's data), dibenzyl does not absorb light in the ultraviolet region of

wavelength greater than 2700Å, corresponding to 106 k.cal./mole. As this is greater than the dissociation energy for any of the bonds in dibenzyl, many modes of dissociation are possible. Obviously, light quanta of such high energy would have a serious effect on the reaction products, and a fast flow system would be required to remove them before their concentration became appreciable. A further drawback existed in the low quantum yield to be expected from this reaction, the considerable back reaction making it unlikely that the yield would be better than 10^{-3}. Thus a lamp of very high intensity would be essential if a measurable decomposition was to be attained. Further inefficiency would be expected due to the low extinction coefficients of dibenzyl, unless a very high pressure of reactant, or a very wide cell, was used.

Despite all the above objections, it was decided to proceed further on these lines as no more suitable approach to the case could be devised, and as there was no hope of applying the method evolved for case 1 for several months. Nevertheless, it was recognised that the difficulties presented above made the chances of success slight.

Figure 22



Photochemical Studies

It was first necessary to prove that photochemical decomposition was possible, and to determine the nature of the products. For this, a small silica cell with plane parallel windows was attached by a silica - pyrex graded seal to a pyrex break-seal and evacuation limb. Sufficient dibenzyl was introduced to supply a vapour pressure of 10 mm. at 250°C. The cell was evacuated, sealed, and placed in a specially constructed electric furnace having an aperture in the side through which light could be directed into the cell (Figure 22). For analysis, ultraviolet spectrophotometry was used.

The optical density of the cell at 250 mμ. was determined before commencing the experiment, using, as a standard, a similar cell containing air at one atmosphere. The cell was placed in the furnace and maintained at a temperature of 250°C. in the dark for 30 minutes, after which its optical density was determined taking care to avoid condensation of dibenzyl on the plane windows. It was then replaced in the furnace and subjected to ultraviolet light from a mercury arc lamp for 60 minutes at 250°C. After measuring the optical density once more, it was subjected to radiation for a further 60 minutes and then left in the dark for 90 minutes at the same temperature. The results are detailed in Table 5.

Table 5

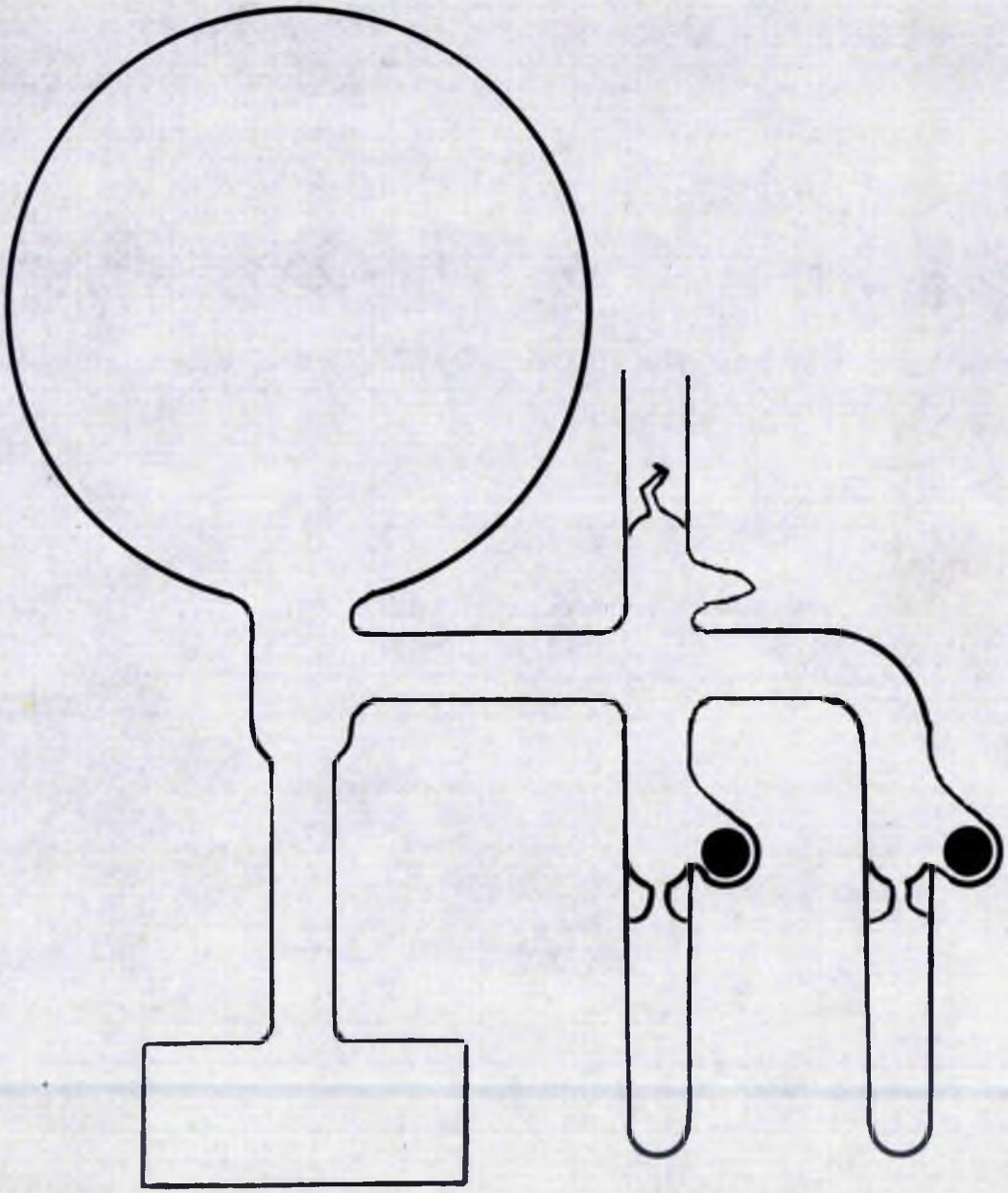
Experiment	Temperature (°C)	O.D.$_{250\ m\mu}$.
Before Starting	25	0.054
½ hr. in dark	250	0.054
1 hr. in U./V. light	250	0.204
1 hr. in U./V. light	250	0.465
1½ hr. in dark	250	0.162

That heat alone caused no change in the optical density of the cell indicates that the thermal reaction was negligible at 250°C. even over a 90 minute period. The effect of ultraviolet light was to increase the absorption considerably, indicating reaction of some form. Continued illumination increased the absorption still further, though the final period of 90 minutes in the dark resulted in a decrease, presumably due to polymerisation of the strongly absorbing products.

To determine the nature of the residual materials, the cell was coupled to the mass-spectrometer, the break-seal fractured, and the volatiles expanded into the sample manifold. A mass-spectrum showed small increases in intensity at the m/e values 91 and 78 indicating the presence of toluene and benzene in very low concentrations. No peak could be found for m/e = 104, the parent ion of styrene, but this was not expected as styrene is extremely sensitive to ultraviolet light.

For a more detailed examination of the reaction products, the simple reaction cell was modified. A 250 ml. pyrex flask was attached to the cell, this remaining outside the furnace, and maintained at 100°C by a heating jacket. (Figure 25). By using this larger volume, it was hoped to increase the quantity of reaction products while reducing their concentration in the light beam. The

Figure 23



starting material was placed in a side tube outside the heated zone and was maintained at a suitable temperature by a constant boiling bath similar to those used with the injection units. A cut-off, consisting of a stainless-steel ball seated in a ground glass socket, isolated the dibenzyl reservoir during the period of illumination. A second side tube and receiver served as a reservoir for the products.

Operation

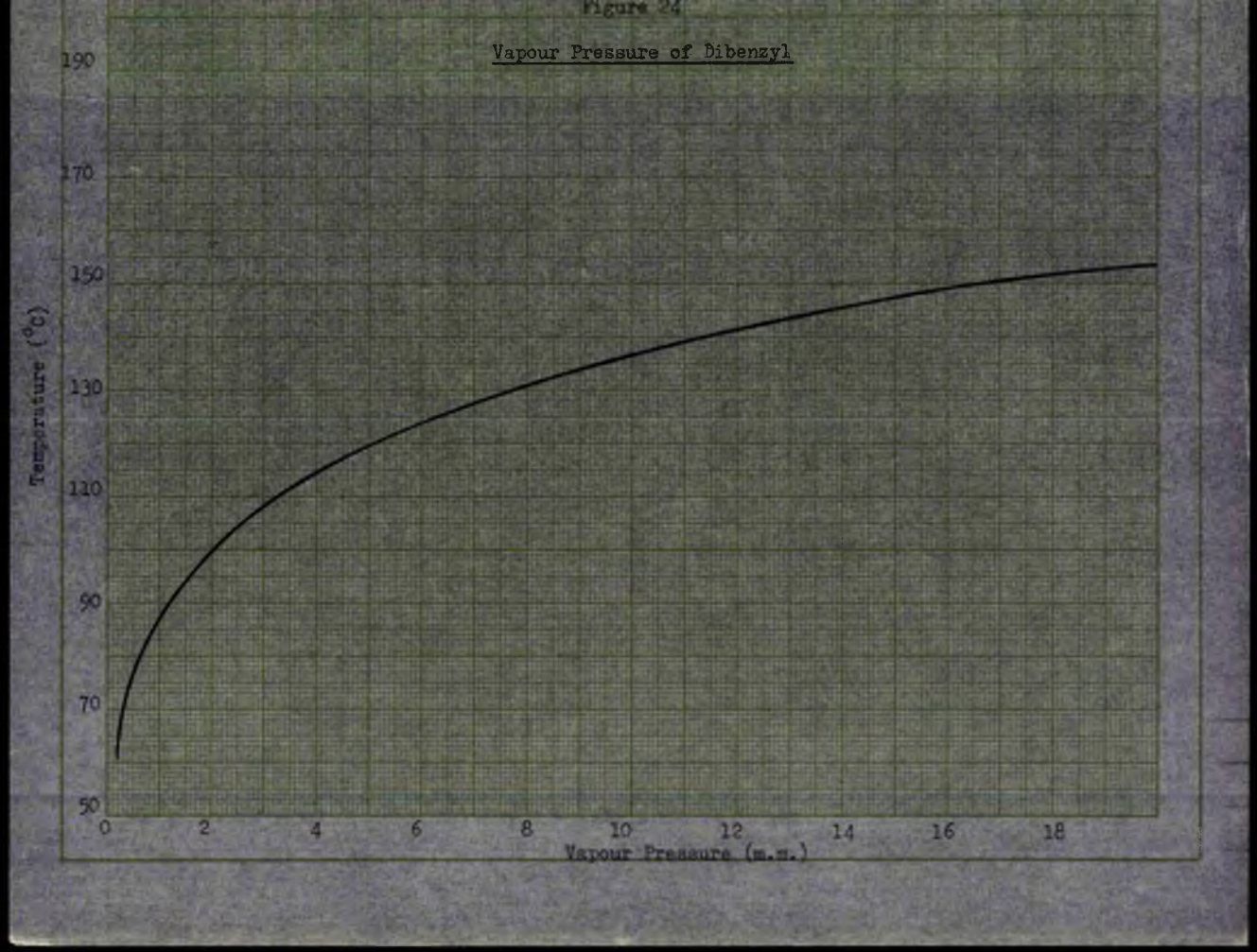
The system was evacuated, sealed, and the receiver cut-off closed. A constant boiling bath was placed round the dibenzyl reservoir, and the cell and expansion volume filled with dibenzyl vapour to the vapour pressure of the heated material. The reservoir cut-off was then closed, after which the shutter to the ultraviolet lamp was opened and the cell illuminated for a measured period. The contents of the cell were then condensed in the receiver and the cycle of operations repeated until a quantity of products, sufficient for analysis, had been collected.

The Vapour Pressure of Dibenzyl

For these experiments, it was desired to maintain a vapour pressure of 0.25 mm. of dibenzyl to reduce to a minimum any undesirable side reactions. A paper had been published on vapour pressures at temperatures below the

Figure 24

Vapour Pressure of Dibenzyl



melting point (46). From this, and the latent heat of fusion of dibenzyl, the vapour pressure curve was calculated for temperatures above the melting point. Previous experience suggested that this curve was seriously in error, and a check on the calculated and true boiling points proved this to be so. The vapour pressure data for liquid dibenzyl quoted by D.R. Stecil (69) was therefore used, and this is shown in Figure 24.

Experimental

Refluxing methanol (65°C) served as the constant temperature medium, delivering a vapour pressure of 0.25 mm. of dibenzyl to the reaction vessel. The cell was illuminated for 60 minutes per cycle, and twelve such cycles were performed for each experiment.

Results

Three runs were performed, and in each case only a trace of toluene could be detected, with no measurable quantity of benzene or styrene. That this minute concentration of toluene was due to the action of light was proved by a blank run in which dibenzyl was maintained at 250°C for 12 hours. No decomposition could be detected at the end of this period.

Ultraviolet spectrophotometry of the involatile materials gave an absorption curve very similar to that obtained for the solid resultants of the thermal reaction,

indicating the presence of stilbene, but not of anthracene or phenanthrene.

The conclusions to be drawn from these experiments were:

(a) that reaction did take place due to the action of ultraviolet light; and

(b) that the products of this reaction did not appear to differ from those of the thermal process.

Attention was then turned to the design of a system which would allow quantitative determination of the reaction products. The requirements were:

(1) A lamp of high intensity in the region 270 mμ. to 250 mμ.

(2) A large area of illumination.

(3) A reaction vessel of considerable depth to allow an appreciable percentage absorption of the light by a low pressure of dibenzyl.

(4) A system wherein all these three requirements could be satisfied, and yet permit the reaction vessel to be raised to 400°C.

The need for exceptionally high intensity in a narrow waveband eliminated the use of a continuous source with a monochromator. Of the discontinuous sources, the most commonly used is the low pressure mercury arc, and as this gives a strong line of wavelength 253.7 mμ. it was consider-

ed to be most suitable for the present work. Moreover, under certain conditions this line can be made to predominate to such an extent that no filter is required to remove undesirable wavelengths. Such characteristics are to be found in the low pressure mercury-rare gas discharge tube described in detail by Melville (48). The important features of this lamp were:

(a) At least 90% of the total emission was at 253.7 mμ.

(b) The total output was of the order of 10^{19} quanta/second, a very high intensity for a single line.

(c) The emission remained constant over long running periods.

(d) Provided the electrode compartments were water-cooled, the temperature of the central portion of the lamp could be varied without varying the output appreciably.

The feature (d) was of special interest for the present work as it would enable the lamp to be placed, with the reaction vessel, inside the electric furnace, and so would eliminate the need for focussing arrangements. The length of the central portion of the lamp was 50 cm. and so would be most suitable for illuminating a reaction vessel of the type used in a flow system. Point (a) was considered very satisfactory as no filtering system would be required. It should be noted, however, that with a similar lamp, quoted by Noyes and Leighton (61), the intensity at 253.7 mμ. amounted to only one quarter of

the total emission, the remainder being at 184.9 mμ. However, the 184.9 mμ. line is very poorly transmitted by fused silica of which material it was intended that both lamp and vessel should be constructed.

As this lamp satisfied most of the requirements, it was decided to adopt it as the light source, but before constructing one, the form of the reaction vessel was considered. Flow systems have been used in which the lamp and reaction vessel are concentric, giving maximum light intensity in the reaction volume. One design by Bates and Taylor (49) has the reaction vessel as an annular jacket surrounding the central portion of the lamp. A second system (50) reverses this arrangement, the outer jacket being part of the lamp. Both systems were used at low reaction temperatures where waxes could be used to make the necessary ring-seals, but for the higher temperatures required for the present study, an all-silica system was necessary, and the technical difficulties involved in the construction of such a combined lamp/reaction chamber unit made it preferable to follow the technique employed by Farkas and Melville (51) in which the lamp is placed alongside the vessel.

The Lamp

Only the long central portion of the lamp was constructed from fused transparent silica. This was a 50 cm. tube of 2 cm. internal diameter, and it was attached to

the water-cooled pyrex electrode-compartments by silica/pyrex graded seals. The compartments, 10 cm. long and 2.4 cm. internal diameter, carried cylindrical electrodes made from nickel sheet, 6 cm. long and having the same internal diameter as the silica portion. A pyrex side tube was attached to permit evacuation of the lamp and admission of samples of neon. A few drops of liquid mercury were placed in one of the compartments.

The Reaction Vessel

This was a 50 cm. tube of transparent silica having an internal diameter of 2.5 cm. Apart from its diameter, it was identical with the vessel used for the thermal experiments, having a 6 mm. diameter re-entrant tube for a thermocouple pocket.

The Furnace

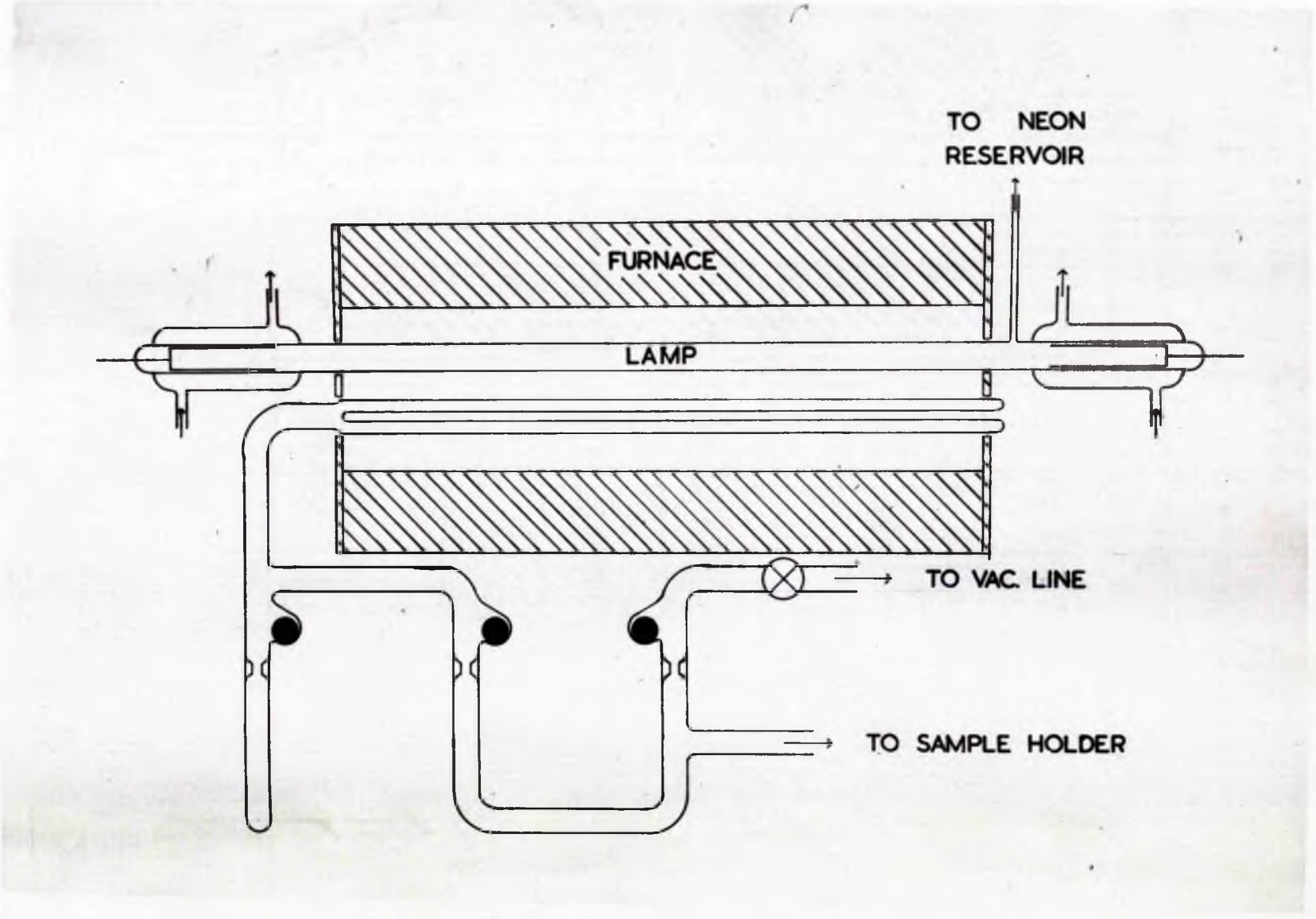
In construction and length this also resembled the thermal system, but was built on a 10 cm. diameter steel tube to afford room for both the lamp and the reaction vessel. "Smoothing" of the temperature profile was carried out as before.

The Static System

Before incorperating these new parts in the flow system, a simple static arrangement was constructed to investigate the performance of the lamp as the position of the furnace at the centre of the flow system made

Figure 25

Photochemical Reaction System



modifications difficult in situ.

The lamp and reaction vessel were placed side by side in the electric furnace the electrode compartments of the former projecting beyond the heated zone (see Figure 25). They were surrounded by a cylindrical aluminium reflector to increase the intensity of light incident on the reaction vessel. To the side arm of the lamp were attached a vacuum line and a narrow line through a Toepler pump to a reservoir of B.C.C. spectrally pure neon. The pressure of the admitted sample was measured with a small manometer and a cathetometer.

For the inlet system to the reaction vessel, a construction was used similar to that employed in the smaller scale static work, with steel balls in ground glass sockets to cut off the dibenzyl reservoir, vacuum line, and sample holder from the reaction chamber. The sample holder, one of those described earlier, (page 68) enabled the volatile products to be removed from the apparatus and transferred to the sample manifold of the mass spectrometer. The line leading from the furnace area to the cut-offs was wound with "Nichrome" tape and heated to 120°C.

Lamp Operation

After evacuating and "baking" the lamp, neon was admitted through the Toepler pump to a pressure of 5 mm. The water cooled terminals were connected to the

secondary coil of 1:10 step-up transformer, the output voltage of which could be controlled by a "Variac" transformer coupled between the primary winding and the mains supply.

A low voltage was applied, and increased gradually until intermittent arcing occurred at about 1500V. Further increases to full output did not produce uniform illumination though it increased considerably the frequency of flashing. This, however, slowly dropped off, and eventually the lamp failed to arc at all. It was then evacuated, and a fresh charge of neon admitted. A very much lower voltage was required to produce arcing on this occasion, and maximum voltage resulted in uniform illumination for several minutes though once more it reverted to intermittent flashing after a while. Several fresh charges were admitted, the lamp being run for 30 minutes with each sample and after four such cycles a stable illumination was obtained at a voltage well below the maximum. An ammeter was coupled in series with the lamp and the voltage adjusted to maintain a constant current of 120 mA.

Experimental Procedure

The apparatus was evacuated, the furnace, outlet heater, and lamp switched on, and the dibenzyl in the small reservoir out-gassed. The cut-off to the sample holder

was closed, a methanol bath placed round the reservoir, and dibenzyl admitted into the reaction chamber. The cut-off to the reservoir was then closed. After two hours, the lamp was switched off and the products condensed in the sample holder. This was transferred to the mass spectrometer and an analysis performed.

Results

The mass spectrum indicated the presence of benzene and toluene, though, unlike the thermal results, benzene showed the higher concentration. The values obtained were:

Benzene 4.8×10^{-6} moles.

Toluene 9.5×10^{-7} moles.

It was also found that the sample holder contained a high pressure of material which was not condensible in liquid air, this being indicated by signs of gas escaping through the mercury seal when the upper portion of the sample holder was being evacuated. Unfortunately the concentration of the remaining material, when expanded into the manifold, was too small to permit characterisation. It was thought, however, that this was methane or hydrogen produced by the action of ultraviolet light on toluene. Such a reaction would account for the high benzene/toluene ratio.

To reduce this decomposition to a minimum, the operational procedure was modified slightly. After the

vapour had been subjected to ultraviolet light for 10 minutes, the U-bend in the vacuum line was cooled in liquid-air to collect the volatile products, and the condensible materials were drawn off by a Toepler pump and collected in a small flask. The volatiles were transferred to the sample holder, a fresh charge of dibenzyl admitted into the reaction chamber, and the process repeated until a total reaction time of two hours had been attained. Both liquids and gases were analysed by mass spectrometry.

Liquids

These consisted of benzene and toluene.

Benzene 4.34×10^{-6} moles.

Toluene 3.08×10^{-6} moles.

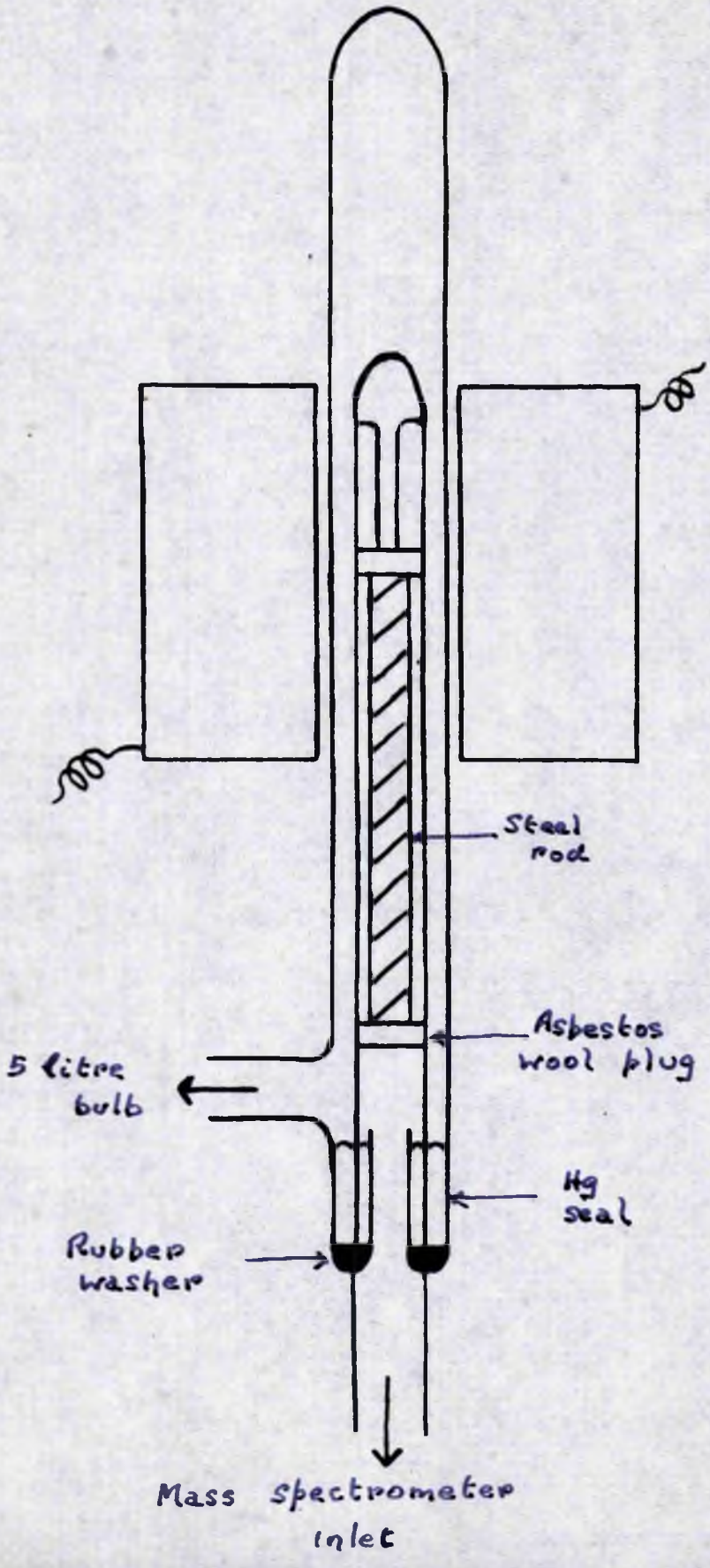
Gases

These were identified as hydrogen with a trace of methane. Accurate quantitative determinations were not attempted as calibrations for hydrogen and methane were not possible without modification of the sample manifold. A rough estimate, made from the pressure of gas in the manifold, gave the total quantity of gases as 3×10^{-5} moles.

Conclusions

By removing the products from the illuminated zone every 10 minutes, the ratio benzene/toluene decreased considerably, offering some justification for the assumption

Fig 2L


Steel rod
Asbestos wool plug
5 litre bulb
Hg seal
Rubber washer
Mass spectrometer inlet

that the high ratio obtained earlier was due to further decomposition of toluene. It was to be expected therefore that if the contact time was reduced from 10 minutes to 1 second by means of a flow technique, the degree of decomposition of the products would be greatly reduced.

It was possible from this to get some indication of the quantities of products to be expected from such a flow experiment. 0.25 mm. of dibenzyl in 179 ml, the volume of the illuminated portion of the reaction vessel, corresponded to 2.1×10^{-6} moles at the reaction temperature of 202°C. The total reaction time was 115 minutes. Hence the rate of decomposition under these conditions was 2.5×10^{-2}% per second. Allowing for a rate of flow of dibenzyl of 10^{-6} moles/second, a run of one hour in a flow system would result in the production of roughly 10^{-6} moles of toluene. The minimum quantity which could be accurately determined on the mass spectrometer with the existing sample manifold was 10^{-5} moles, so it was necessary either to increase the length of run by a factor of ten, or to increase the sensitivity of the analyses. The latter possibility was considered more practicable.

Modification to the Sample Manifold

To increase the sensitivity of the mass spectrometer, a small solenoid cut-off was constructed and was coupled in the lead to the expansion volume (Figure 26). When

this was closed, the effective volume of the manifold was reduced 15 fold, the sample being expanded into the small volume of the cut-off valves and the lead only. In this way, quantities as small as 10^{-6} moles could be determined to within 2%.

Procedure

With the cut-off shut, the sample was expanded into the manifold, and the heights of the various peaks determined. After the vapour had been condensed in the side arm, the cut-off was raised and a measured pressure of nitrogen admitted to determine the sensitivity of the instrument. For calibration, the cut-off was kept open, and a measured sample fifteen times greater than the unknown sample was admitted and scanned as before. A conversion factor was then applied to give the quantity of sample in the smaller portion of the manifold.. This conversion factor was determined by measuring the peak heights of m/e = 28 for a sample of nitrogen confined to the small volume and expanded into the large volume. It was found to be

Small Volume = Large Volume x 0.0666.

The Flow System

The furnace and reaction vessel of the thermal system (see Figure 2, page 40) were replaced by the new furnace, reaction vessel and lamp described in this section. The experimental procedure was identical with that followed in

the previous flow work. With the exception of the temperature range and the presence of ultraviolet light, the conditions used corresponded closely to the thermal runs.

Twelve twenty minute runs in the temperature range 200°C - 350°C indicated a serious drift in results depending on the "age" of the neon in the lamp. It appeared that the nature of the emission altered with time, and this was confirmed by the increase in visible radiation observable after several hours of operation.

Actinometry

Following the procedure adopted by Melville, the mercury photosensitised decomposition of gaseous ammonia was used to study the emission variations. Pure dry ammonia was made by dropping 0.880 ammonia solution on to quicklime in a 3 litre flask, passing the gas through columns containing quicklime and potassium hydroxide pellets, and collecting in a liquid air trap. The collected material was further purified by repeated distillation at -80°C and stored in a 3 litre reservoir.

Ammonia was passed through a "bubbler" containing mercury into the reaction vessel to a pressure of 100 mm., and illuminated for a measured period. The remaining ammonia was then collected in a liquid-air trap and the decomposition products, nitrogen and hydrogen were collected in a small

volume by means of a Toepler pump, the pressure being measured with a McLeod gauge. As the mercury photo-sensitised decomposition of ammonia is temperature dependent, this method could not be used to determine variations in intensity with furnace temperature, but it was successful for intensity variations with time at a fixed temperature.

At the same time, a modification was made to the lamp. The cooling water for the electrode compartments was supplied from a thermostat bath instead of from the water main, and the water temperature was adjusted to give maximum intensity. As it was considered possible that the "ageing" effect might be due to impurities evolved from tap grease, the lamp was filled with a fresh supply of neon and sealed off from the supply line.

The degree of decomposition of ammonia was determined before and after each run, and the average of the two readings taken as a measure of the intensity of the lamp. It was found that after the lamp had been sealed off from the neon supply little variation of intensity with time could be detected at any temperature used.

Results

A series of runs was performed in the temperature range 220°C - 300°C. As the significance of these is discussed later (page 145) only a brief summary will be

given at this stage.

In no case did toluene appreciably exceed benzene, the ratio benzene/toluene varying from 1 to 3 unsystematically. This variation makes the significance of the results very dubious as it would appear that toluene was lost by decomposition. A plot of log. (rate of formation of toluene) against $1/T^{\circ}K$ gave a value of 0 ± 0.5 k.cal./mole for the apparent activation energy of the radical-molecule reaction whereas there are good reasons (see page 159) for believing that the process will be endothermic by a few k. calories. Applying this to the equation:-

$$E_{obs.} = E_a + \tfrac{1}{2} \triangle H$$

we get $47.6 = 0 + \tfrac{1}{2} \triangle H$

$\therefore \quad \triangle H = 95.2$ k.cal./mole.

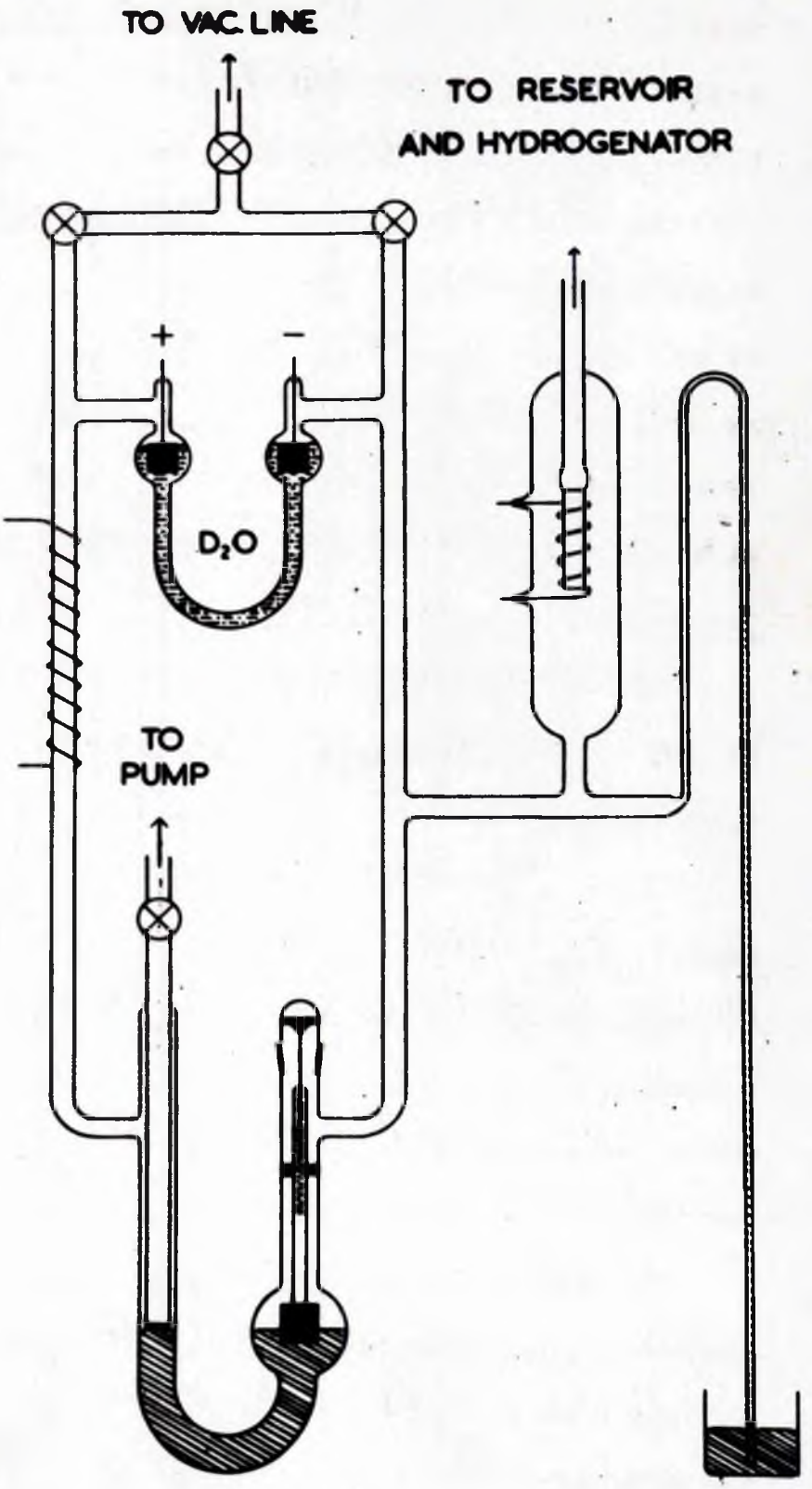
Thus, assuming zero activation energy for the recombination of benzyl radicals, the activation energy for the reaction $Ph.CH_2.CH_2.Ph \longrightarrow 2Ph.CH_2.$ would be 95.2 k.cal./mole. This is clearly too high and the method must be recognised as unsatisfactory.

The Direct Determination of $\triangle H$.

The indirect approach having failed to give reliable data, attention was turned once again to the possibility of applying the technique outlined earlier (page 91) to

Figure 27

Electrolysis Apparatus



the direct determination of ΔH. The high resolution mass spectrometer had not been completed, and it was realised that it would not be in operation before the period allotted for the present work had expired. Nevertheless, though the existing mass spectrometer was incapable of good resolution in the required mass region, it was decided to proceed as far as possible, and obtain as much information as that instrument could give on the possibility of applying the technique at some later date when the more accurate instrument became available.

Preparation of Deuterated Dibenzyl

The simplest conceivable process for the preparation of deuterated dibenzyl would be by the deuteration of diphenyl acetylene

$$Ph.C{\equiv}C.Ph + 2D_2 \longrightarrow Ph.CD_2.CD_2.Ph$$

using Adams catalyst. It is known that in such processes exchange reactions can also occur and might result in the substitution of deuterium in the phenyl rings. The extent of such action could not be predicted and consequently trials had to be made.

The deuterium was prepared by the electrolysis of deuterium oxide (99.97% purity) and purified by diffusion through a heated palladium thimble. Figure 27 illustrates the apparatus employed. A solution of 20% D_2SO_4 in D_2O was placed in the electrolytic cell, the apparatus was

evacuated, and a current of 125 mA allowed to pass. The cathode compartment was coupled to a small reservoir carrying, on a re-entrant arm, a palladium thimble heated to dull redness by a spiral of "Nichrome" wire. The purified deuterium was collected in a Toepler pump and transferred to a storage bulb coupled directly to a simple hydrogenator. A water jacket was placed round the cell to prevent boiling of the liquid.

To maintain equal pressures at the two electrodes, the oxygen liberated at the anode was pumped away through a manostat, the compensating limb of which was coupled to the cathode compartment. The cut-off point of this manostat could be adjusted by displacement of the mercury on the cathode side by a steel plunger mounted on a threaded shaft. Careful adjustment of this ensured automatic control of the liquid levels in the cell to within 5 mm.

In the early stages, trouble was experienced due to the formation of ozone at the anode, causing immediate "tailing" of the mercury in the manostat and blockage of the sinter. This was eliminated by winding a short length of the outlet from the anode with "Nichrome" tape and heating to 400°C at which temperature the ozone was spontaneously decomposed.

As it was essential to have less than 1% of hydrogen

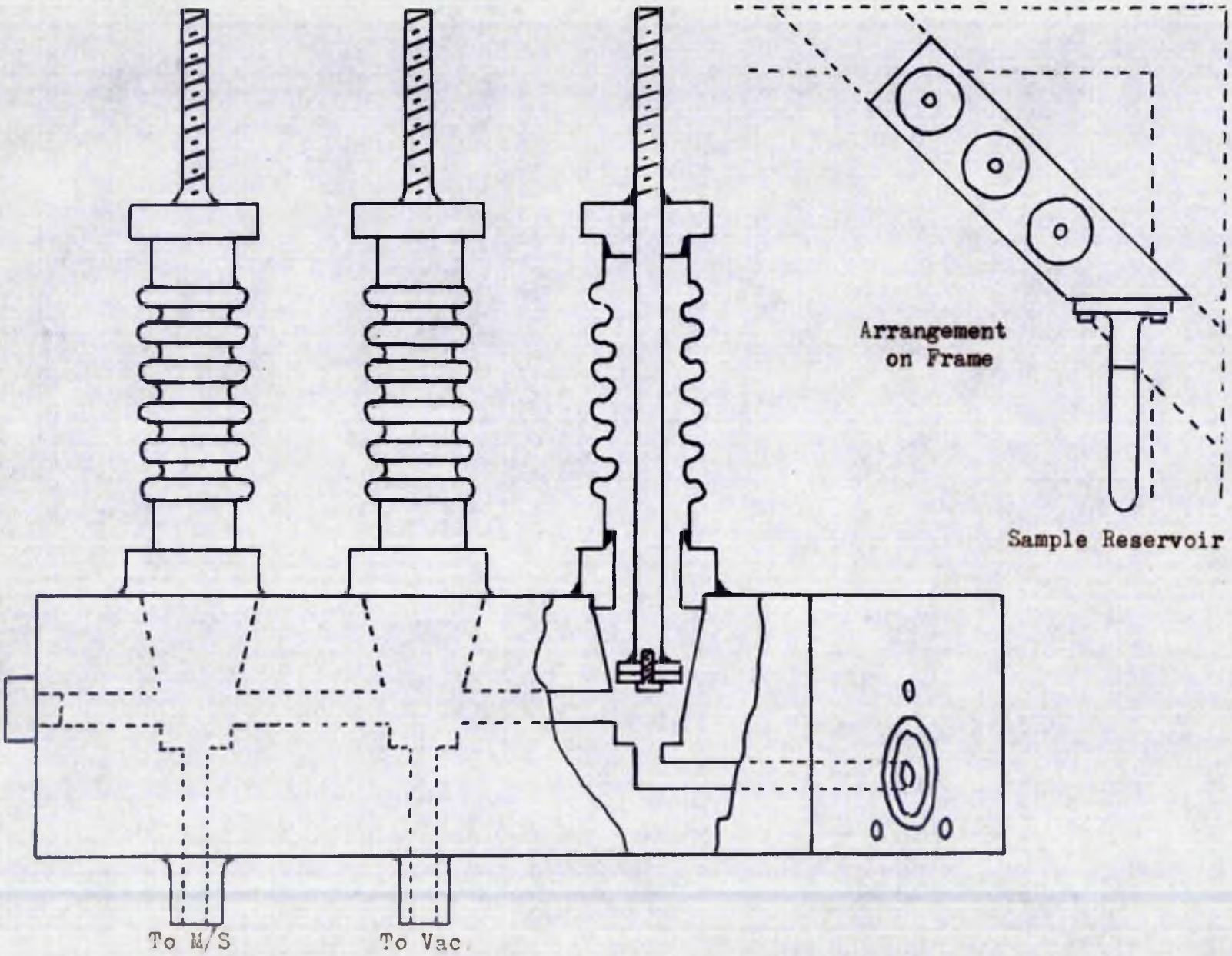
in the gas evolved at the cathode, care was taken in the preparation of the electrolyte. Sulphur trioxide was prepared by distillation at atmospheric pressure from fuming sulphuric acid, and was purified by passing through a series of drying tubes containing phosphorus pentoxide and by vacuum distillation. It was then allowed to distil slowly into deuterium oxide until the required concentration had been reached. A mass spectrometric study of this solution failed to detect the presence of the ion H^+ indicating that less than 0.25% of H_2O existed.

2 gm. of pure diphenyl acetylene were dissolved in 150 ml. of dry methanol together with 150 mgs. of Adams catalyst, and deuterated at one atmosphere. Initially the reaction went very quickly, 90% of the deuterium being taken up in one hour, though the removal of the last traces of deuterostilbene required 2 - 3 days. The product was recrystallised twice before its purity was checked by ultraviolet spectrophotometry. The absorption spectrum indicated the presence of deuterostilbene to somewhat less than 1%, which was considered unimportant for the intended work.

Diphenyl acetylene was prepared by the bromination of stilbene followed by treatment with alcoholic potassium hydroxide, and purification by fractional crystallisation.

Figure 28

Solids Handling System



The Solids Handling System

As the vapour pressure of dibenzyl is 10^{-4} mm. at room temperature, a system of cut-offs and inlet leak which could operate at temperatures as high as 150°C were required. A set of three all-metal valves was therefore constructed, the design being similar to that employed for the injection units, but using "Teflon" discs seated on steel as the cut-off agents. The details are illustrated in Figure 28. The basis of all three valves was a single block of steel 8" x 2" x 2", the cut-off chambers and side arms being bored out of the solid to eliminate several brazed joints. The unit was mounted at an angle of 45° on one corner of the mass spectrometer frame with the valve shafts in the horizontal plane, and heated to the required temperature by windings of "Nichrome" tape. The sample was placed in a glass tube attached by a metal to glass seal to a flange which was then bolted to the block with a "Teflon" washer. A bath containing boiling water maintained a constant pressure of dibenzyl in the system.

Calibrations were attempted with the glass inlet line to the ionisation chamber, and the analyser tube, at room temperature, since the pressure beyond the "Metrosil" leak was very much less than the vapour pressure of dibenzyl, but it was found that adsorption on the walls was so considerable that the instrument did not respond until 15

minutes after the sample had been admitted, and only reached equilibrium after 30 minutes. The whole of the analyser and inlet system was therefore heated to 80°C, after which stability could be attained in less than 5 minutes.

Constitution of the Deuterated Dibenzyl

With a resolution of 1 in 80, good resolution of masses in the region 180 - 190 could not be expected. Moreover, at that time no reference standard for dibenzyl was available, so it was necessary to do some preliminary work on dibenzyl. This showed that the benzyl radical ion was produced in greater profusion than the parent ion $Ph.CH_2.CH_2.Ph^+$. By analogy with toluene, it was expected that the ion $Ph.CH.CH_2.Ph^+$ might predominate, but the spectrum disproved this. The data of the American Petroleum Institute Project 44, which became available later, agrees with these findings and gives the following relative abundances for the various ions.

Mass No.	91	178	179	180	181	182	183
Relative Abundance	100	0.91	0.62	0.24	0.09	19.1	2.96

Thus, in the high mass region, the parent ion peak is very prominent and the isotope peak 183 is not sufficiently large to interfere seriously. It is reasonable to assume that the characteristics of the spectrum of deuterated dibenzyls would not differ greatly

from this pattern.

The problem with deuterated species lies not in their spectra, but in their molecular constitution. During catalytic deuteration, exchange reactions take place with the hydrogen atoms already present in the molecule, resulting in the formation of appreciable quantities of HD. This in turn can saturate a double bond giving the molecule $Ph.CHD.CD_2.Ph$. Thus it is possible to visualise a series of compounds with varying numbers of deuterium and hydrogen atoms in the aliphatic group as well as further types where deuterium has entered the aromatic nucleus.

The simplest and most satisfactory system for the present purpose would be the pyrolysis of a mixture of $Ph.CH_2.CH_2.Ph$ and $Ph.CD_2.CD_2.Ph$ in equal proportions. The initial reactions

$$Ph.CH_2.CH_2.Ph \longrightarrow 2Ph.CH_2.$$

$$Ph.CD_2.CD_2.Ph \longrightarrow 2Ph.CD_2.$$

would be followed by recombination of the radicals resulting in the formation of some of the species $Ph.CH_2.CD_2.Ph$. Thus, by following the rate of appearance of this compound, a measure of the rate of decomposition of dibenzyl could be obtained.

With a mixture of deuterated compounds such as is obtained from the catalytic deuteration of diphenyl

acetylene, the method can still be applied. Obviously if compounds such as $Ph.CH_2.CHD.Ph$ or $Ph.CH_2.CD_2.Ph$ are present in the mixture, their concentration will not be altered when pyrolysed in the presence of dibenzyl, but others such as $Ph.CHD.CHD.Ph$ will appear in the resultants in lower concentration with a corresponding increase in $Ph.CH_2.CHD.Ph$. The net result of pyrolysing the deuterated mixture with dibenzyl should be a lowering of the concentrations of the higher masses with a corresponding increase in the lower masses. At the same time, the concentration of dibenzyl as measured by the intensity of the 182 peak should decrease considerably. Thus by following the variations in intensity of the masses 182, 183 and 184 a measure of the reaction should be possible.

Experimental

The modifications made to the flow system for the photochemical experiments were removed, and the original reaction vessel and furnace replaced. A 1:1 mixture of dibenzyl and deuterated dibenzyl was placed in the reservoir of one of the injection units, and a run performed using reaction conditions which were identical with the earlier thermal work, and at a temperature of 635°C. The solid products from this run were transferred to the solids handling manifold and a mass spectrum obtained.

Interpretation of the spectrum was hindered by the uncertainties introduced when using a low resolution

instrument. When a large peak exists alongside an unresolved small peak, the latter appears as a minor fork or peak on the side of the former. The magnitude of this minor peak is enhanced by the spread of its neighbour, making quantitative estimation extremely difficult. However, by maintaining strictly comparable conditions it is possible to use such a spectrum in a quantitative fashion.

A preliminary examination of dibenzyl showed that this gave the expected pattern, 182 being the principal peak in the high mass region. Deuterated dibenzyl gave relative intensities as shown below.

Mass No.	182	183	184	185	186
Intensity.	42.6	81.0	100.0	82.4	20.6.

This shows that the deuterated material contained mainly molecules having 1 to 3 deuterium atoms per molecule. No attempt has been made to correct these figures for overlap of adjacent peaks.

In the 1:1 mixture of dibenzyl and deuterodibenzyl, the figures before and after heating were:

Mass No.	182	183	184	185	186
Intensity Before.	100	46.6	59.1	31.3	17.2
Intensity After.	100	84.0	41.9	19.4	9.7

These figures refer to the relative intensities of the peaks where the intensity of the peak at mass number

Table 6

Temperature (°C)	Ratio $\frac{181^+}{183^+}$	Calculated % Decomposition
366	2.10	~ 0
450	2.00	6
523	2.00	67
638	1.54	100
706	1.53	100
723	1.53	100

182 is taken as 100, and should not be confused with absolute intensities which could not be determined.

From this it seems that pyrolysis brings about an increase in the proportion of the 183^+ and 184^+ ions together with a decrease in the intensities at 185 and 186. This is in accord with the production of mixed dibenzyls by randomisation of radicals.

A series of runs was performed maintaining all conditions except temperature constant, and varying the latter from 556°C to 725°C. As a measure of randomisation, the ratio $182^+/183^+$ was used, and the results are listed in Table 6 together with the calculated percentage decompositions from the equation $k(sec^{-1}) = 10^{13} e^{\frac{(-45000)}{RT}}$. This assumes that the rate determining step in the randomisation is the rate of dissociation of dibenzyl, and that first order conditions are obeyed. The results show the rough temperature limits within which randomisation appears to commence and reach completion.

The method is clearly capable of providing significant evidence on the dibenzyl reaction, using a sufficiently sensitive mass spectrometer. However, with the available equipment it is very valuable as a method of discriminating between the two conflicting values obtained by other methods. Using a bond energy value of 69 k.cal./mole, the calculated decomposition would be a small fraction of

1% at 650°C, assuming a temperature independent factor of 10^{13}. This is not in agreement with the present findings. A bond dissociation energy of 45 k.cal./mole corresponds fairly closely with the data, as can be seen from Table 6.

After the above work was completed, Mr. I.M.T. Davidson reconstructed the ion gun and ion collecting system of the mass spectrometer tube, and attained the desired resolution of 1 in 200. He has kindly provided the following figures for a 1:1 mixture of dibenzyl and deuterated dibenzyl.

Mass No.	182	183	184	185	186
Intensity.	100	45.7	34.4	19.0	8.6

This confirms the previous, less accurate, findings.

DISCUSSION

Summary

The opening pages of this section are devoted to a review of the evidence revealed by the various experimental techniques which have been applied to the problem.

The relationships between the several products and their variations with temperature and pressure have been illustrated graphically and the significance of these changes discussed. The lack of stoichiometric balance is also considered and some possible explanations proposed.

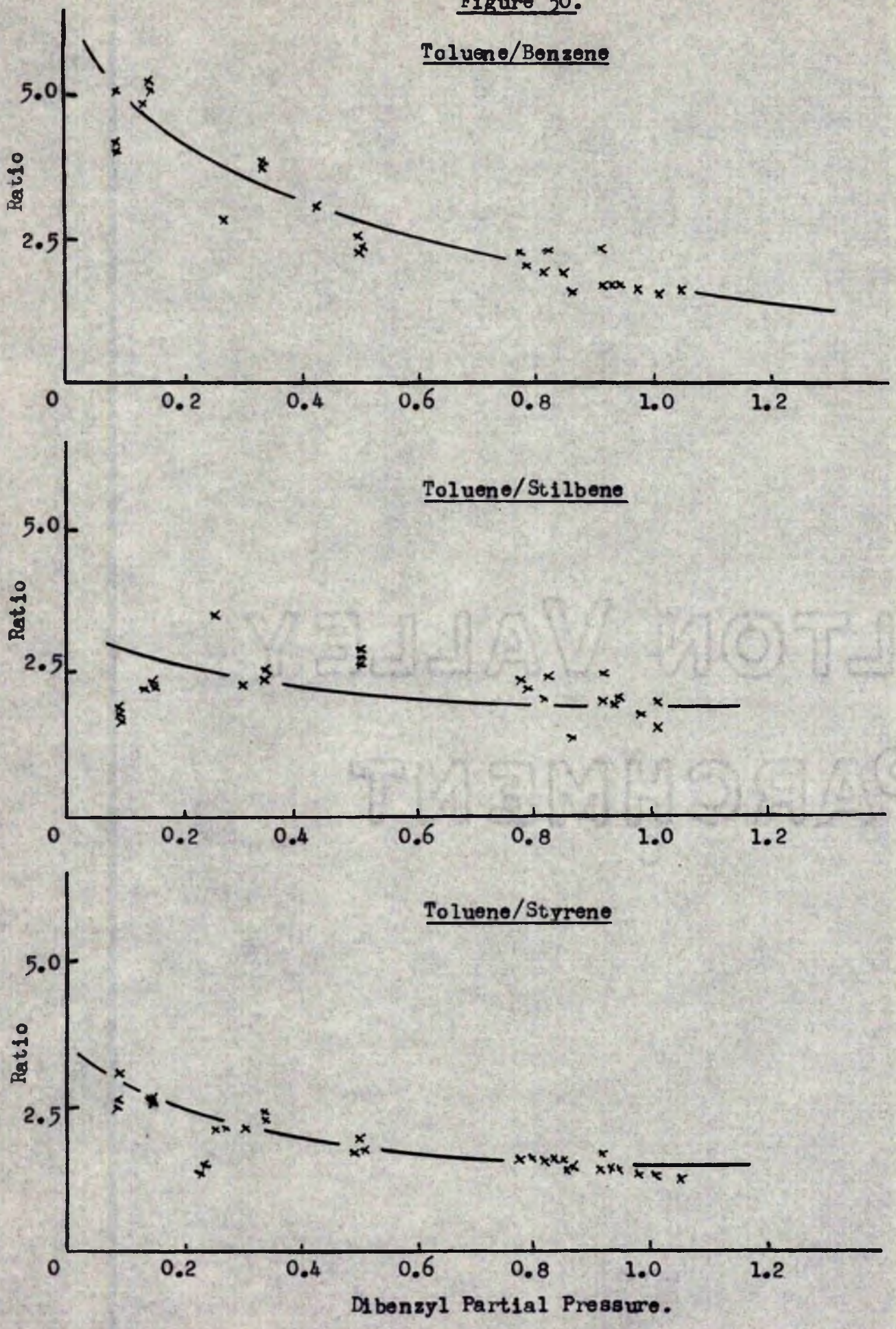
This is followed by an outline of the various mechanisms which are available for the production of the resultants in the observed quantities, and the relative merits of these are discussed. On the basis of this discussion a value is proposed for the dissociation energy of the central C-C bond.

The final section is concerned with the conclusions which can be drawn from this value regarding the energies involved in other steps of the reaction and their significance in the general scheme of bond energies.

The Experimental Evidence

It has been stated earlier in this thesis (page 90) that although the qualitative evidence pointed to a 1.5 order dependence for the rate of formation of toluene, the

Figure 30.

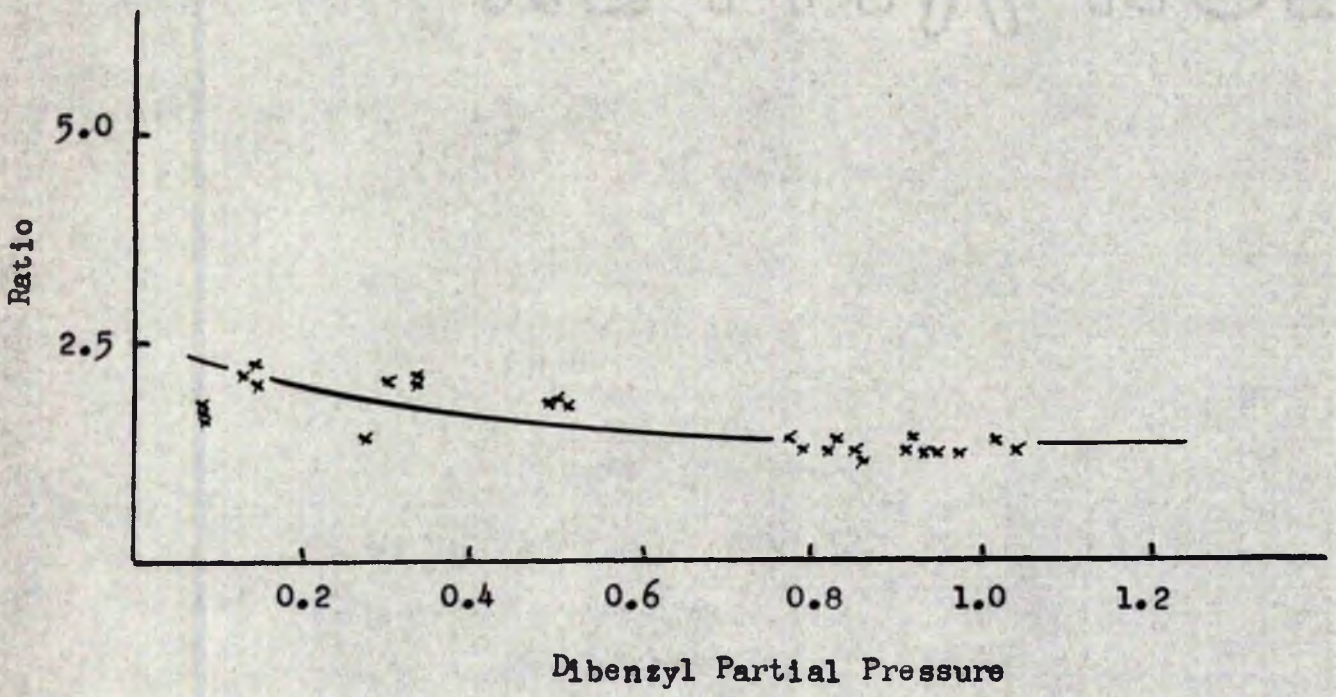

Toluene/Benzene
Ratio
5.0
2.5
0
0.2
0.4
0.6
0.8
1.0
1.2
Toluene/Stilbene
Ratio
5.0
2.5
0
0.2
0.4
0.6
0.8
1.0
1.2
Toluene/Styrene
Ratio
5.0
2.5
0
0.2
0.4
0.6
0.8
1.0
1.2
Dibenzyl Partial Pressure.

quantitative data indicated that true 1.5 order behaviour was not followed. A plot of toluene formation against partial pressure showed an excessive decrease in rate with decreased pressure of dibenzyl. It was important, therefore, to determine the behaviour of the other, possibly secondary, products under these conditions, as variations in the quantities of these might throw some light on the unexpected results.

The details of the partial pressure experiments have been compiled in the form of a graph (Figure 30) in which the ratios of benzene, styrene, and stilbene to toluene have been plotted against partial pressure of dibenzyl. It is evident that the constant ratio benzene:toluene: styrene observed by Horrex and Miles cannot be found here. At high partial pressures (0.5mm.-1.0mm.) there is a rough approximation to constancy, but the divergence at low pressures is considerable. This divergence is most serious for the benzene/toluene curve though the others also exhibit some degree of variation. As the pressure decreases the proportion of toluene to benzene increases rapidly, an increase of more than 2.5 fold over the pressure range covered by the experiments. From stoichiometric considerations it would be expected that the proportion of styrene would also rise. The separation of a phenyl group from a dibenzyl molecule would leave a

Figure 31.

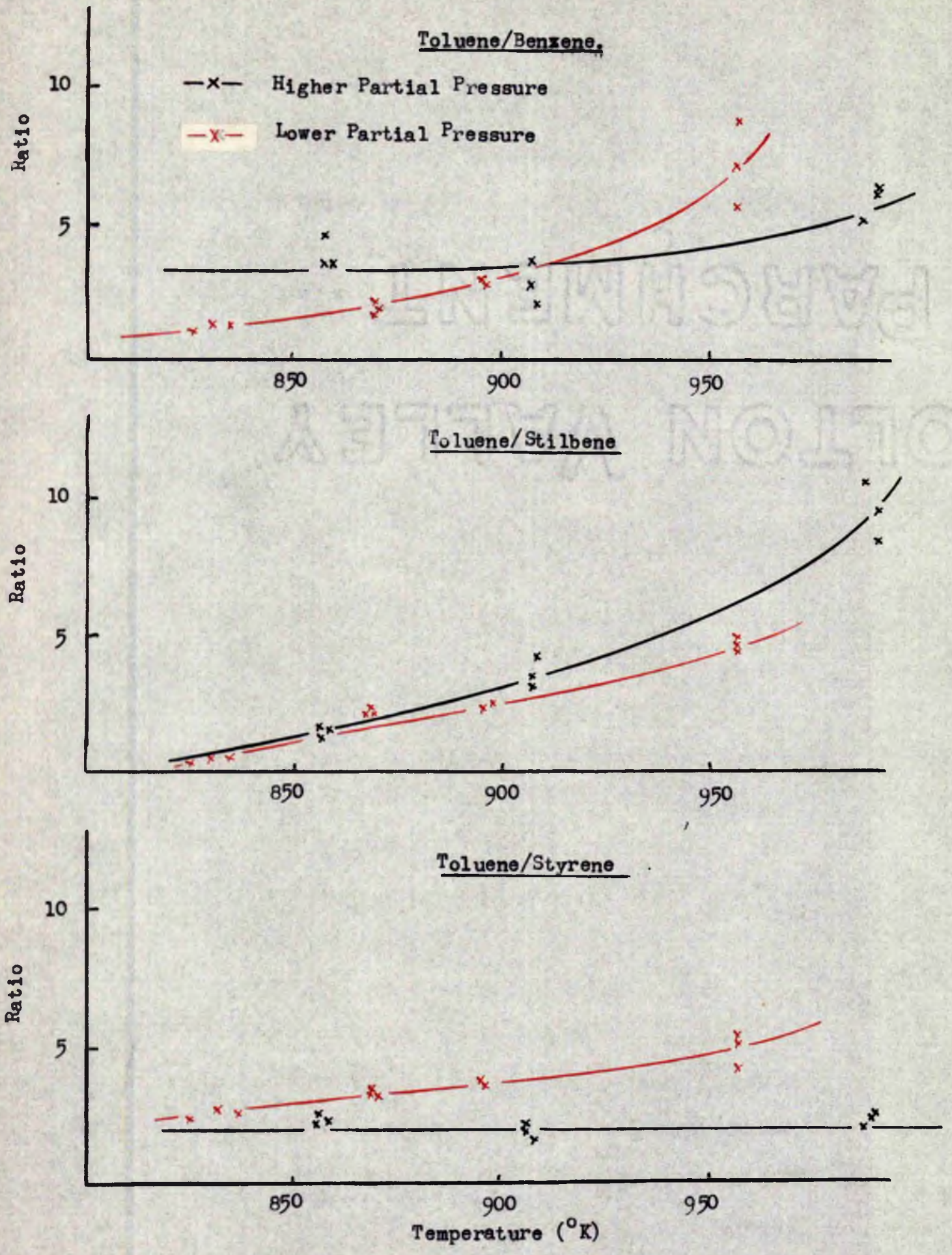
Styrene/Benzene



residue which could produce ethylbenzene or styrene, and the former has been found to be absent. The phenyl group would be expected to appear as benzene since there was no evidence of other products containing a single phenyl unit or of appreciable amounts of diphenyls. The toluene/styrene curve does exhibit a slight rise, but it does not in any way correspond to that of benzene. The factor here is only 1.5. Thus there would appear to be an appreciable concentration of phenyl groups unaccounted for in the resultants. Figure 31 illustrates this loss of benzene by a plot of the ratio Styrene/benzene against partial pressure of dibenzyl. It can be seen from this that the balance approaches unity at partial pressures of 0.5 mm. and over, but below this the curve rises considerably. It would appear, therefore, that a close approximation to a stoichiometric balance obtains at high pressures, while at low pressures the divergence is serious.

The behaviour of the various products with change of temperature exhibits similar anomalies. The available evidence is outlined in Figure 32 in the same manner as was used for the partial pressure results. These curves bear a striking resemblance to each other, similar divergences occurring for low pressures and high temperatures. Here, however, there is no region of constancy

Figure 32.


Toluene/Benzene.
Higher Partial Pressure
Lower Partial Pressure
Ratio
10
5
850
900
950
Toluene/Stilbene
Ratio
10
5
850
900
950
Toluene/Styrene
Ratio
10
5
850
900
950
Temperature (°K)

comparable with the high pressure results of Figure 30. Instead, all ratios rise increasingly with temperature, and only styrene exhibits a fairly flat curve. Whereas in the partial pressure curves the toluene/benzene graph shows a striking rise at the low pressure end of the scale, the other two curves remaining fairly flat, in the temperature curves all three ratios rise several fold with increased temperature, and benzene does not stand out as exceptional. It is the behaviour of styrene that differs here, the toluene/styrene remaining much lower than either of the others.

Summary

At low pressures, the proportion of benzene in the resultants decreases by a factor of 2.5, though those of the other products remain fairly constant. From 0.5mm. - 1.0 mm. the constancy reported by Norrex and Miles obtains approximately.

The study of temperature variation reveals the fact that the increase in toluene production with temperature is out of all proportion to the other products. Styrene production follows fairly closely, but benzene and stilbene proportions fall off steeply. Figure 32 and Table 11 show that there is no actual drop in rate of formation of these latter compounds with temperature, but the rate of increase is small in comparison with that of toluene.

From this evidence it would appear that there exists some means by which benzene or the phenyl radical is converted to some unidentified product or products, and also a method of increasing the toluene formation beyond expectation.

One possibility lies in the chance of the formation of diphenylmethane if phenyl radicals take part in the reaction sequence. The absence of diphenylmethane could not be demonstrated by the available techniques, and so this possibility should be held in view. The concentration of radicals would be small and the possibility of collision poor in comparison with the chance of hydrogen abstraction from dibenzyl. It is therefore unlikely that this biradical reaction would be preferred to the extent suggested by the low pressure results, unless the concentration of benzyl radicals was exceedingly high.

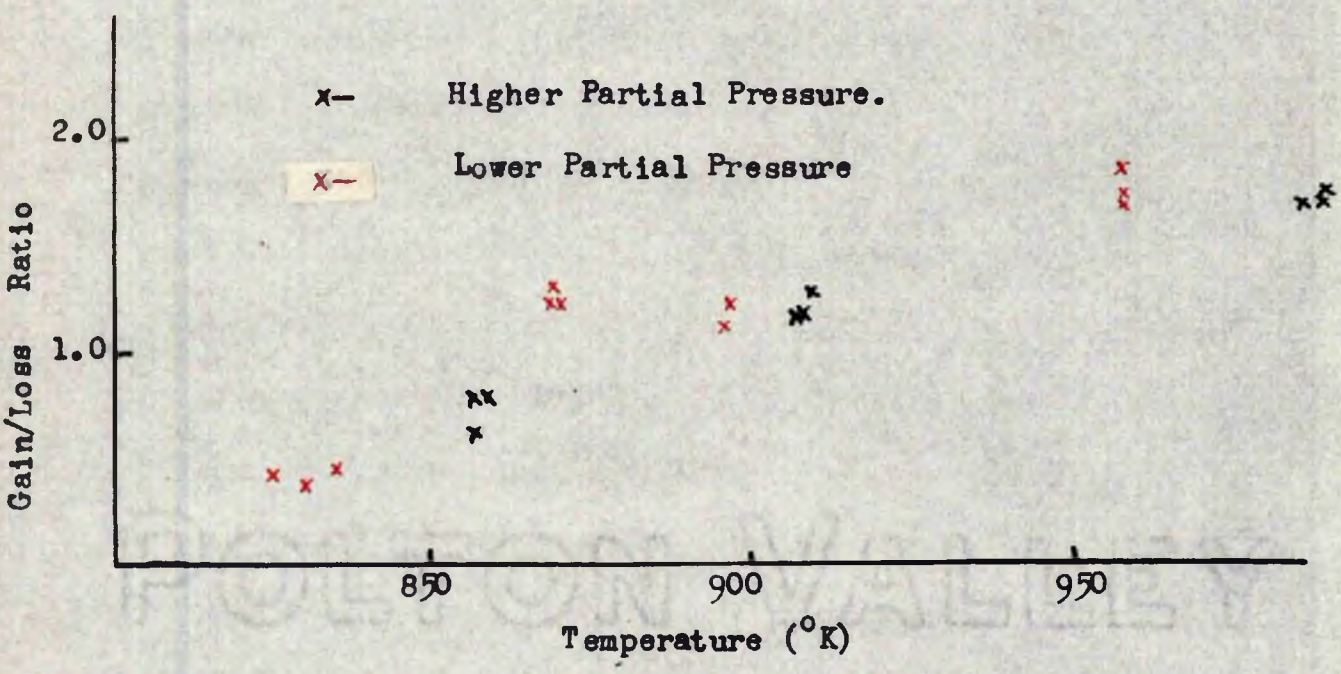
A third, and more promising cause, can be found in the work of C.F. Cowan (53) on the pyrolysis of phenyl iodide. Cowan found that pyrolysis of this compound, using essentially the same flow technique and gas pressures as in this work, resulted in an appreciable deposit of carbon on the wall of the reaction vessel. The addition of about a millimetre pressure of toluene as a radical acceptor diminished this effect, but did not eliminate it. The effect was ascribed to the migration of phenyl

radicals to the wall where they decomposed to elemental carbon and hydrogen. In order to stop this diffusion, it was found that the carrier gas pressure had to be raised to over 400 mm. nitrogen. This ensured reaction with 1-2mm. of toluene which was also present. Such an effect demonstrates the surprising lack of reactivity of the phenyl radical towards an efficient radical acceptor.

In a similar way, if phenyl radicals are involved in the decomposition of dibenzyl, it is unlikely that the parent compound, though itself a better radical acceptor than toluene, would be capable of deactivating all the radicals before they collided with the chamber wall. At high pressures of the parent substance this effect would be a minimum, but at low pressures it would be expected that an appreciable proportion of the radicals would reach the wall and decompose. An increase in temperature would also enhance this effect, and reduce the proportion of benzene formed. The result of such a process would be the deposition of carbon and the formation of free hydrogen. Little deposition was observed, but the quantities involved are so small that little would be expected. The absence of hydrogen in the gas stream is, at first sight, a serious drawback to this theory.

If it is supposed that the phenyl radicals which were unaccounted for decomposed to carbon and hydrogen on the wall, and that all the free hydrogen atoms formed

Figure 33.


Higher Partial Pressure.
Lower Partial Pressure
2.0
1.0
Gain/Loss Ratio
850
900
950
Temperature (°K)

molecular hydrogen, the pressure rise in the apparatus could not go undetected at high temperatures, though it might not be noticeable at low partial pressures. But in the high temperature runs the drop in benzene formation is accompanied by a rise in toluene formation, a rise which cannot be accounted for by normal hydrogen abstraction reactions. Figure 33 shows the Gain/Loss ratio for hydrogen exchange.: the Gain value is the sum of hydrogen atoms obtained by benzyl and phenyl radicals to form toluene and benzene: the Loss value is the sum of styrene plus 2.(stilbene), this giving the number of hydrogen atoms which must be lost from dibenzyl to form these substances. From this it can be seen that the hydrogen gained rises to almost twice the observable loss from conventional sources. Thus more than half the gain is unexplained. Considering Run No.40, one of the highest temperature experiments, we see that the apparent loss of benzene, judged from the styrene collected, is 7.44×10^{-8} moles/l. The Gain/Loss ratio for this run is 1.80, and therefore of the 2.70×10^{-7} moles/l. of toluene collected, 1.20×10^{-7} moles/l. remain unexplained. If all the lost phenyl radicals decomposed to the elements there would be available a total of 3.72×10^{-7} gm. atoms/l. of hydrogen. This is three times the amount required to form the extra toluene. It is likely there-

fore that a combination of this effect with the formation of some diphenylmethane could account for the anomalies observed in the quantitative analyses. The traces of hydrogen noted in an analysis of the incondensibles can also be justified.

This suggestion presupposes the participation of phenyl radicals in the reaction sequence, though no direct evidence of such was obtainable.

The Mechanism

There can be little doubt of the initial steps of the reaction sequence. The results of the dibenzyl-fluorene experiments clearly indicate that benzyl radicals are involved in the mechanism, and that the rate of formation of these is very much greater than the corresponding rate of formation of toluene. Thus a back reaction of the form:

$$2Ph.CH_2. \longrightarrow Ph.CH_2.CH_2.Ph$$

is unquestionably present. Moreover, since the plot (rate of formation of toluene)/(partial pressure of fluorene) at constant temperature and partial pressure of dibenzyl (see Figure 17, page 85) shows a straight line dependency on fluorene concentration, the concentration of benzyl radicals is not lowered by the rate of their removal as toluene in these experiments.

Two procedures have been proposed to account for this.

(1) The decomposition to benzyl radicals is very high, and recombination and further reaction do not occur in the furnace area but take place in the cooler outlet.

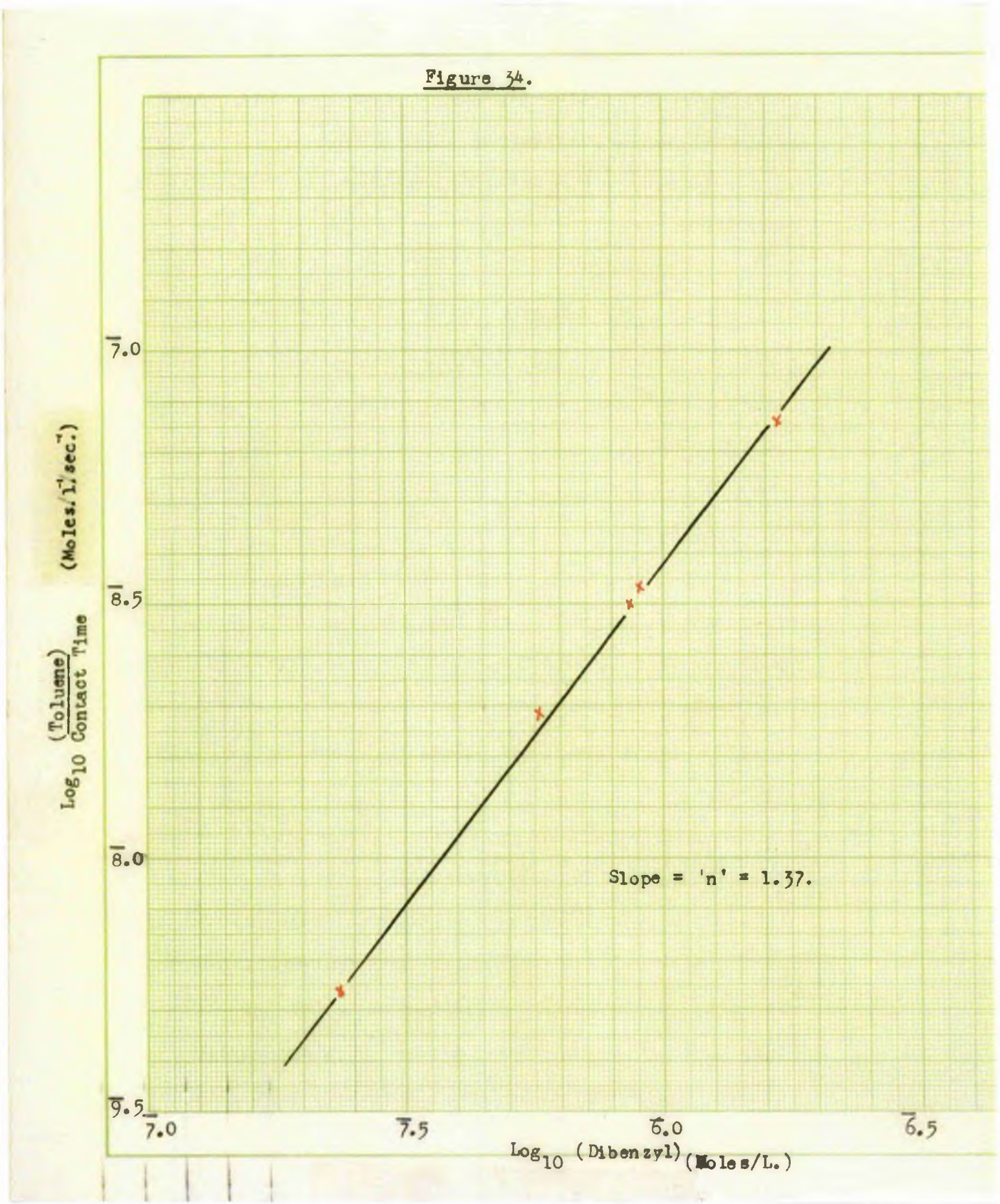
(2) The rate of decomposition and the rate of recombination are both very high, and the result is a small equilibrium concentration of radicals. In effect this is equivalent to a reaction of the form

$$Ph.CH_2.CH_2.Ph \longleftrightarrow 2Ph.CH_2.$$

Of these suggestions case (1) is unsatisfactory, as it is unlikely that the presence of such a large concentration of radicals would result in so small an increase in toluene production when fluorene is introduced. The addition of an equimolecular proportion of fluorene causes the rate of formation to increase by a factor of 3.1 only. On the other hand, if case (2) is operative this small increase would seem more plausible as dibenzyl and fluorene would be competing for benzyl radicals on equal terms, and a factor of 3.1 is reasonable for two hydrogen donors where the energies of abstraction may differ by two or three k.cal./mole.

It has been demonstrated that case (2) would lead to a 1.5 order law with respect to toluene formation, yet the plot $k_{1.5}$/partial pressure of dibenzyl at constant temperature in the absence of fluorene (Figure 20, page 90)

Figure 34.


$\overline{1}$7.0
$\overline{1}$8.5
$\overline{1}$8.0
$\overline{1}$9.5
$\log_{10}$ (Toluene / Contact Time (Moles/L/sec.))
7.0
7.5
6.0
6.5
$\log_{10}$ (Dibenzyl) (Moles/L.)
Slope = 'n' = 1.37.

shows that the calculated 1.5 order rate constant is not independent of partial pressure. The apparent order of reaction is in fact somewhat lower than 1.5.

Since 'n', the order of reaction, is defined by the equation:

$$\frac{dx}{dt} = k.a^n$$

$$\text{then } \log.\frac{dx}{dt} = \log.k + n.\log.a$$

Thus a plot of the log. of the rate of formation of toluene against the logarithm of the partial pressure of dibenzyl injected should give a straight line whose slope is 'n'. This has been done in Figure 34 and a value of 'n' = 1.37 was obtained.

However, from the evidence of the flow-rate work alone, it is clear that the proposition is basically sound, and that the reaction must proceed through a steady state concentration of benzyl radicals caused by the rapid decomposition of dibenzyl and an almost equally rapid recombination.

Any doubts on this score are removed on considering the results of the mass spectrometric studies of the dibenzyl - deuterodibenzyl mixtures. Using temperatures well below the range for appreciable toluene formation there is evidence of a randomisation of the components. Some idea of the relative rapidity of this reaction can be obtained by observing the temperature region in which

"equilibration" occurs - i.e. where randomisation is complete. Table 6 shows that this situation is reached at approximately 638°C, a temperature corresponding to 0.39% decomposition to toluene. Hence, the rates of formation and recombination of benzyl radicals are many times greater than the rate of their reaction with dibenzyl to form toluene.

From this evidence, the principal reaction of the mechanism can be established as

$$Ph.CH_2.CH_2.Ph \longleftrightarrow 2Ph.CH_2.$$

Despite this confirmation of the initial processes, the failure to conform more accurately to a 1.5 order law remains unexplained. The assumption was made that the steady state concentration of benzyl radicals was small, but even if this was not so, it could not account for the apparent 1.37 order dependence. For, if at any moment

x = the amount of dibenzyl decomposed to toluene etc.

y = the dibenzyl dissociated to benzyl radicals.

a = the dibenzyl injected.

then (a-x-y) = the undissociated dibenzyl.

$\therefore$ the rate of formation of toluene $= k_a.2y.(a-x-y)$ 1.

now $K = \dfrac{4y^2}{(a-x-y)}$ 2.

$\therefore 2y = K^{\frac{1}{2}}.(a-x-y)^{\frac{1}{2}}$ 3.

$\therefore \dfrac{dx}{dt} = k_a.K^{\frac{1}{2}}.(a-x-y)^{3/2}$ 4.

The experimental data have been applied to the equation

$$\frac{dx}{dt} = k_{obs.}(a-x)^{3/2} \qquad 5.$$

$$\text{thus } k_{obs.}(a-x)^{3/2} = k_a.K^{\frac{1}{2}}(a-x-y)^{3/2} \qquad 6.$$

$$\text{or } k_{obs.} = k_a.K^{\frac{1}{2}}\left(1 - \frac{y}{a-x}\right)^{3/2} \qquad 7.$$

Now, from equation 2, the concentration of radicals depends on the square root of the dibenzyl concentration, and hence at low pressures of dibenzyl the fraction dissociated would be higher than at high pressures.

i.e. $\frac{y}{a-x}$ would decrease with increasing pressure of dibenzyl.

$\left(1 - \frac{y}{a-x}\right)$ would increase with increasing pressure of dibenzyl, and reach a limit of unity at higher pressures. Thus, if the concentration of benzyl radicals was appreciable, the observed rate constants, calculated from equation 5. would be lower than the true rate constant at the low pressures and tend to approach the true, or higher, value at high pressures. This is the reverse of the observed behaviour for dibenzyl (Figure 20).

An explanation can be found if the suggestion, made in the first section of this chapter, is adopted, viz. that phenyl radicals are involved in the mechanism. A study of the graphs of product ratios indicates that the production of toluene is too complex to have a simple order

ascribed to it. If phenyl radicals do decompose on the wall, the toluene formation has no longer a simple kinetic dependence on the concentration of dibenzyl, but is altered appreciably by the reaction of hydrogen atoms produced in this side reaction. At low pressures the proportion of toluene to the other resultants is increased, and hence the rate of production is higher than would be calculated assuming a 1.5 order dependence. At higher pressures the secondary effect is considerably reduced, giving a closer approximation to the expected order.

In consequence of this complex behaviour, it is obvious that a study of the rate of formation of toluene can yield little satisfactory information regarding the energy changes accompanying the various reactions. However, the isotope method has provided a satisfactory technique for the study of the equilibrium reaction independent of the secondary processes. It is unfortunate that the available equipment was insufficiently sensitive to allow quantitative work in this field, for accurate observations of the rate of randomisation would have yielded the rate of dissociation of dibenzyl to benzyl radicals, and hence the activation energy for the reaction

$$Ph.CH_2.CH_2.Ph \longrightarrow 2Ph.CH_2.$$

Yet with the rough work which was performed it is

possible to determine which of the two conflicting values in the current literature is the more accurate. Although the exact heights of the various peaks in the mass spectrum of the isotope mixture could not be measured, the temperature range in which a change could be detected in the composition of the collected material was readily obtained.

In Table 6, the changes in composition with temperature are shown, the composition change being measured by the ratio of peak heights $\frac{182^+}{183}$. Alongside this are listed the calculated percentage dissociations of dibenzyl at these temperatures using the equation $k(sec.^{-1}) = 10^{13} e^{\frac{(-45000)}{RT}}$. The correspondence between the two columns is fairly close whereas no relationship could be shown between the experimental data and values calculated using a bond dissociation energy of 69k.cal./mole.

Thus it can be stated that, of the two conflicting values, that calculated from Szwarc's observations on toluene is corroborated by the present information, whereas that calculated from Steacie's conclusions is not supported in any way. Hence it is justifiable to ascribe a value of approximately 45 k.cal./mole. to the dissociation energy of the bond $Ph.CH_2 - CH_2.Ph$.

Since it has been established that benzyl radicals

participate in the reaction mechanism, and since one section of the investigation has indicated that fluorene can act as an effective radical acceptor for these radicals, it is justifiable to assume that this ability also obtains with dibenzyl.

(a) $Ph.CH_2\cdot + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH_3 + Ph.CH.CH_2.Ph$

The presence of an equimolecular proportion of fluorene in dibenzyl has been shown to bring about a 3 fold increase in toluene formation, and this is in line with the C-H bond energies for the two compounds. The C-H bond energy in dibenzyl would, by analogy, be expected to have a value intermediate between those of toluene and fluorene, viz. between 77.5 and 68.8 k.cal./mole. A rough estimate of 70 k.cal./mole for D(Ph.CH-H.CH_2.Ph) would not be in error by more than one or two k.cal. Hence, if fluorene can act as a radical acceptor, it is highly probable that dibenzyl will behave likewise. This certainly is not the only path by which toluene is made, especially at low pressures and high temperatures, but it would account for the greater part at high pressures.

Unfortunately the fluorene experiments yield no information regarding the formation of the other products. So far as could be determined, there was little alteration in the rates of formation of these when high concentrations of fluorene were introduced. Since the steady state

concentration of benzyl radicals was unaffected by their rate of removal as toluene, if the rates of formation of the products are connected directly or indirectly to the concentration of benzyl radicals, the presence of fluorene would not influence these reactions in any way. Thus there is no indication whether these reactions are of a secondary nature, or occur independently.

If the formation of toluene occurs by reaction (a), it is necessary that at least one of the other observed final products should result from secondary processes as reaction (a) produces the radical $Ph.CH.CH_2.Ph$ and no trace of tetraphenyl butane, the dimer, could be found.

Many reaction systems can be proposed, whereby the conversion of this radical can explain the occurrence of the products found, but unfortunately the available evidence is insufficient to substantiate any of these suggestions fully. The possibilities are listed below, and an attempt is made to evaluate the relative merits of each of the proposed steps.

Of the simple single-stage processes available to the $Ph.CH.CH_2.Ph$ radical the following must be considered. The associated energy changes have been deduced using standard heats of formation for the molecules, and derived radical heats of formation. The approximate value used throughout for $D(Ph.CH-H.CH_2.Ph)$ is 70 k.cal./mole. The

values used, and the methods of calculation, are listed in the appendix.

(b) $Ph.CH.CH_2.Ph \longrightarrow Ph.CH{=}CH.Ph + H$ −58.1 k.cal.

(c) $H + Ph.CH_2.CH_2.Ph \longrightarrow Ph.H + Ph.CH_2.CH_2\cdot$ +10.9 k.cal.

(d) $Ph.CH_2.CH_2\cdot \longrightarrow Ph.CH{=}CH_2 + H\cdot$ −36.1 k.cal.

(e) $Ph.CH.CH_2.Ph \longrightarrow Ph.CH{=}CH_2 + Ph\cdot$ −66.7 k.cal.

(f) $Ph.CH_2.CH_2.Ph + Ph\cdot \longrightarrow Ph.H + Ph.CH.CH_2.Ph$ +30.7 k.cal.

(g) $2Ph.CH.CH_2.Ph \longrightarrow Ph.CH{=}CH.Ph + Ph.CH_2.CH_2.Ph$ +12.4 k.cal.

(h) $H + Ph.CH_2CH_2.Ph \longrightarrow Ph.CH.CH_2.Ph + H_2$ +53.5 k.cal.

(i) $H + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH_3 + Ph.CH_2\cdot$ + 32.5 k.cal.

The system (b),(c),(d), is a sequence which gives all the required products, but involves a chain mechanism of which there is no evidence from the experimental results. By this approach there should be equimolecular proportions of toluene and stilbene, while benzene and styrene should occur in considerable excess. Moreover, (b) would appear to be ruled out on energetic grounds as it would require an activation energy of at least 58 k.cal./mole.

For the formation of stilbene, the disproportionation reaction (g) would be more satisfactory, as it is exothermic to the extent of 12 k.cal. though it offers no

related path for the formation of the other products. Energetically it is more satisfactory than (b), though it would follow a second order law. Reactions (e) and (f) provide an alternative path for the production of styrene and benzene, but here also a chain system is involved. However, if stilbene results by disproportionation involving two of the radicals $Ph.CH.CH_2.Ph$ as in (g) the chain length might not be great if reaction (g) was efficient, as propagation is based on the reformation of this radical. Like (b), it is highly endothermic. It has the advantage of including the participation of phenyl radicals, which would permit an explanation of the anomalous behaviour of toluene and benzene at low pressures etc.

Two alternative reactions to the chain system (c), (d) are (h), (i), both of which are more highly exothermic than (c). (h) is a hydrogen abstraction reaction which leads to the radical $Ph.CH.CH_2.Ph$ and a molecule of hydrogen. The exothermicity of 33 k.cal. is higher than (i), but experimental observations indicate (h) cannot occur in any great quantity. (i) would satisfactorily explain the absence of hydrogen, and at the same time give support to the theory that the excessive rate of production of toluene at low pressures and high temperatures is due to the disruption of phenyl radicals.

The absence of hydrogen has been a serious drawback to this theory, but (i) offers a method for the removal of hydrogen atoms which is at least comparable with (h). The benzyl radical formed in this reaction would not affect the mechanism, as it would be absorbed in the equilibrium dibenzyl <—> benzyl. (i) would be more probable than the radical recombination

(j) $Ph.CH_2\cdot + H\cdot \longrightarrow Ph.CH_3$

as the concentrations of these are small. There is, however, no apparent reason for such a strong preference for path (i) rather than (h).

It is conceivable that the explanation for the absence of hydrogen from the products could lie in a combination of two or more of these reactions in such a way that the intermediate hydrogen atom never had, at any time, an independent existence, but was transferred directly during a bimolecular collision process.

(k) $Ph.CH.CH_2.Ph + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH{=}CH.Ph + Ph.CH_3 + Ph.CH_2\cdot$ -25.8 k.cal

(l) $Ph.CH.CH_2.Ph + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH{=}CH.Ph + Ph.H + Ph.CH_2.CH_2\cdot$ -47.2 k.cal

(m) $Ph.CH_2.CH_2\cdot + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH{=}CH_2 + Ph.CH_3 + Ph.CH_2\cdot$ -3.8 k.cal

Of these, (k) would permit the formation of excess toluene without the intervention of hydrogen atoms, but would not account for the loss of benzene as determined

from the styrene content. The system (l),(m) provides a mechanism for the formation of all the secondary products from the radical Ph.CH.CH_2.Ph and also gives an extra quantity of toluene, but, like (k) it does not explain the anomalous benzene concentration. These suggestions have the advantage of permitting the formation of excess toluene without the need for a postulate involving the disruption of phenyl radicals, but they have several disadvantages. Not only are they unsatisfactory for the reasons already mentioned, but it is also difficult to see why either (k) or (l)-(m) should be more active at low pressures where the toluene concentration shows a considerable increase. It is equally difficult to visualise the complex electronic transitions which would be necessary for such a system. Yet the fact that free hydrogen atoms are not involved could be held to be in their favour.

Neither of the two values obtained for the overall activation energy of toluene formation can yield any useful information, as each was obtained from experiments performed in the low pressure region where the approximation to 1.5 order behaviour is poor.

If, however, a series of experiments was run at a pressure of dibenzyl greater than 0.5 mm., the activation energy determined in this range would have more value.

Above 0.5 mm., the complexities of the reaction are greatly reduced, and the principal steps can be written as:-

$$Ph.CH_2.CH_2.Ph \xleftrightarrow{K} 2Ph.CH_2.$$

$$Ph.CH_2. + Ph.CH_2.CH_2.Ph \xrightarrow{k_a} Ph.CH_3 + Ph.CH.CH_2.Ph$$

followed by deactivations of the radical $Ph.CH.CH_2.Ph$. Thus the rate of formation of toluene is governed by the relation

$$\frac{d(Toluene)}{dt} = k_a.(Ph.CH_2.).(Ph.CH_2.CH_2.Ph)$$

Now, since the initial decomposition of dibenzyl to benzyl radicals is an equilibrium reaction,

$$(Ph.CH_2.) = K^{\frac{1}{2}}.(Ph.CH_2.CH_2.Ph)^{1/2}$$

Thus

$$\frac{d(Toluene)}{dt} = k_a.K^{\frac{1}{2}}.(Dibenzyl)^{1.5}$$

This we can equate to the experimental relation

$$\frac{d(Toluene)}{dt} = k_{obs.}(Dibenzyl)^{1.5}$$

i.e. $k_{obs.} = k_a.K^{\frac{1}{2}}$

$$E_{obs.} = E_a + \tfrac{1}{2}\triangle H.$$

where E_a is the activation energy for the radical attack on the parent molecule, and $\triangle H$ is the equilibrium reaction heat for Dibenzyl ⟷ Benzyl.

Hence, with satisfactory values for $E_{obs.}$ and $\triangle H$, an activation energy can be calculated for the radical attack. Alternatively, if E_a could be determined independ-

ently, it would serve as a further check on $\triangle H$.

The Photochemical Experiments

For this attempt to give a successful evaluation of E_a, the activation energy for radical attack on dibenzyl, it was necessary that certain conditions be fulfilled.

(1) With the exception of the initiation stage $Ph.CH_2.CH_2.Ph \longrightarrow 2\ Ph.CH_2\cdot$, the reaction mechanism should proceed parallel to the mechanism of the thermal runs.

(2) The presence of ultraviolet light should not affect the products appreciably.

It is obvious from the results that one or both of these conditions did not obtain. The percentage decompositions were so small (about 0.1%) that the quantities of resultants after runs of 30 minutes were difficult to measure. The ratio of stilbene to dibenzyl was such that no accurate estimation of the concentration of the former could be achieved.

Benzene and toluene were present in measurable quantities, but the styrene concentration was negligible. This lack of styrene was not unexpected, as it is readily polymerised under the influence of ultraviolet light.

As far as could be detected, therefore, the products

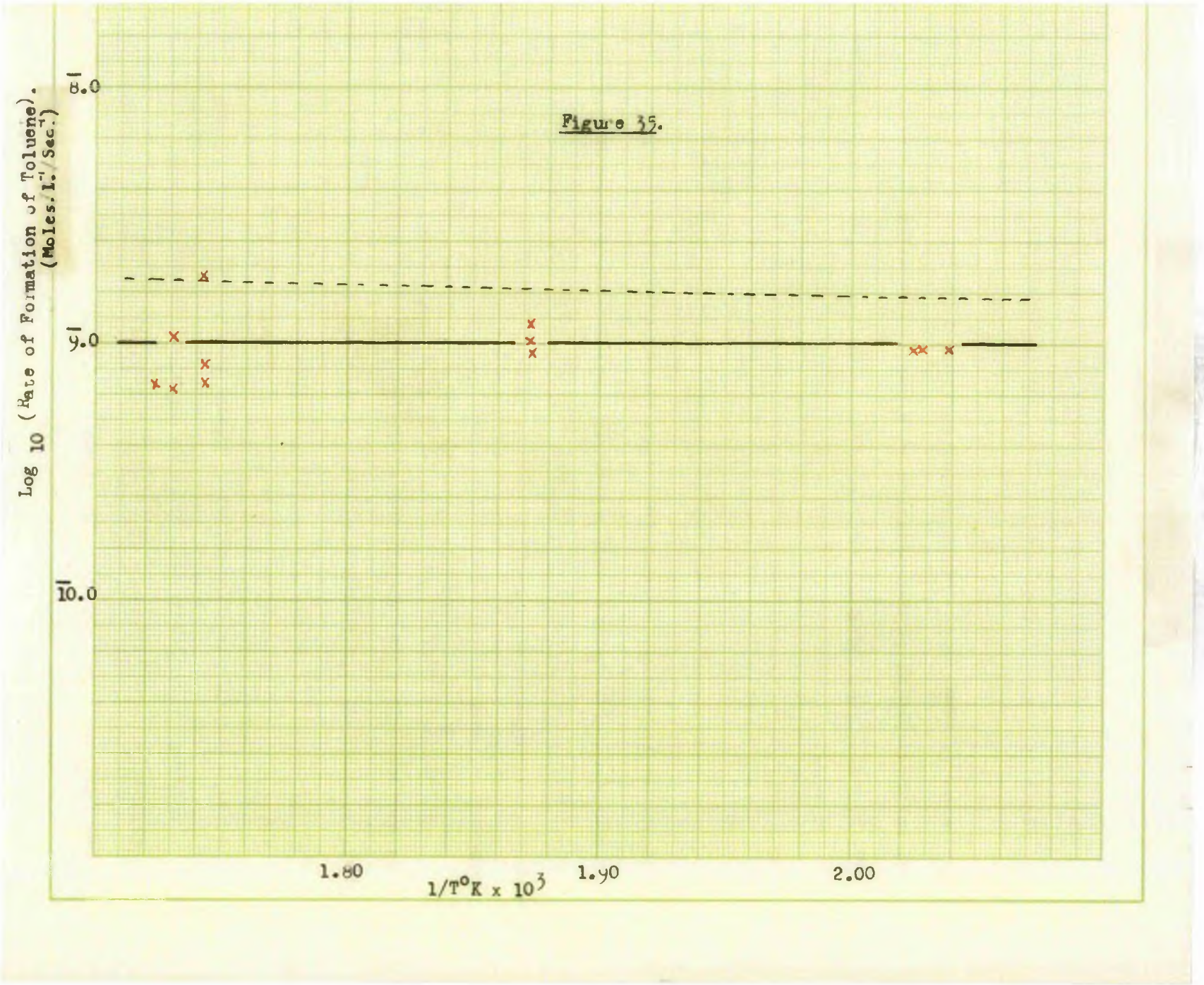


Figure 35.
Log 10 (Rate of Formation of Toluene). (Moles. l.⁻¹/Sec.⁻¹)
8.0
9.0
10.0
1.80
1.90
2.00
1/T°K x 10³

agreed qualitatively with the thermal experiments. Quantitatively, however, the correspondence failed, and relative concentrations of the two directly determinable components, benzene and toluene, exhibiting a marked irregularity in their relationship, and having a ratio toluene/benzene varying from 2/1 to 1/3 approximately.

This irreproducibility and marked excess of benzene makes the results extremely suspect. It is probable that the large proportion of benzene was caused by further reaction of toluene under the influence of ultraviolet light, but there is also the possibility that the reaction mechanism followed a path unrelated to the thermal process. A thorough investigation of the reaction system would have been required to elucidate this, and unfortunately the time available at that period would not permit extensive work in this field.

As a result of the general uncertainty, it is not possible to draw any definite conclusions regarding the activation energy E_a of the radical/molecule reaction. However, a graph has been drawn (Figure 35) plotting the logarithm of the rate of formation of toluene against the reciprocal absolute temperature. The slope of this line is horizontal or nearly so, indicating an apparent activation energy very close to zero. Even if there were losses of toluene to benzene caused by ultraviolet

light, correction for this would not alter the slope and consequently the activation energy, appreciably, as can be seen from the interrupted line in Figure 35 for which the rate of formation of toluene+benzene is plotted.

These results would seem to indicate an activation energy of less than 1 k.cal./mole. for the formation of toluene by the attack of benzyl radicals on dibenzyl. The reaction $Ph.CH_2\cdot + Ph.CH_2CH_2Ph \longrightarrow Ph.CH_3 + Ph.CH.CH_2Ph$. is, however, likely to be endothermic to the extent of 7 k.cal./mole. and so its activation energy must be at least equal to this value.

If, by further work, the true mechanism of this reaction could be elucidated, then the method may offer some possibilities for the determination of E_a, but the complications introduced by the sensitivity of the products to ultraviolet light make this doubtful.

Summary

A. A re-examination has been made of the pyrolysis of dibenzyl at low partial pressures of reactant and of carrier gas. The aim of the first stage was to confirm the stoichiometry previously postulated

$$3\,Ph.CH_2.CH_2.Ph \longrightarrow 2\,Ph.CH_3 + Ph.CH{=}CH.Ph + Ph.H + Ph.CH{=}CH_2$$

and to check the kinetic expression

$$k(sec^{-1}) = 10^{9.3}\exp.(-46.0\ k.cal.)/RT.$$

produced in that work.

B. Analytical techniques have been more extensive than in the previous investigation and have involved the use of mass-spectrometry and ultraviolet spectrophotometry.

C. The products observed previously, namely toluene, benzene, styrene, and stilbene, have been confirmed as the significant resultants. Their ratios, however, were not confirmed and the stoichiometry of the equation above was found to hold over a limited range only.

The variations in the proportions of the products have been studied at 630°C over the range 0.085mm. to 0.85mm., of dibenzyl, and at 0.3mm. over the temperature range 584°C to 716°C, and the results are illustrated in Figures 30 and 32.

D. The previous work assumed that the rate of dissociation of dibenzyl was rate determining, and on this assumption first order rate constants were calculated. In spite of the discrepancies in the stoichiometry noted in C. the results of this work show that the pyrolytic data are more satisfactorily fitted by the equation

$$\frac{dx}{dt} = k_{1.5}(a-x)^{1.5}$$

This implies that the rate determining step is the rate of attack on the parent hydrocarbon by benzyl radicals, and not the rate of formation of the latter.

E. The prediction (from the 1.5 order noted in D.) that

an equilibrium

$$Ph.CH_2.CH_2.Ph \longleftrightarrow 2Ph.CH_2.$$

is set up rapidly has been examined in two ways.

(a) Fluorene has been shown to be an effective trap for benzyl radicals and in its presence the production of toluene from dibenzyl was increased several fold.

(b) The rate of randomisation in a mixture of dibenzyl and deuterated dibenzyl has been shown to be very much more rapid than the rate of formation of toluene, and to take place appreciably at temperatures at which toluene formation could not be detected.

F. The general temperature dependence of the production of toluene noted in the previous work was confirmed.

In view of the stoichiometric variations noted in C. and the closer correspondence with order 1.5 noted in D., deductions of significance from energies of activation are difficult. Even if the stoichiometric difficulties could be solved, the values of $K_{1.5}$ available at the various temperatures could only lead to

$$E_{1.5} = \triangle H/2 + E_a,$$

where

$\triangle H$ = the bond dissociation energy of dibenzyl to two benzyl radicals.

E_a = the energy of activation for the secondary reaction of a benzyl radical with the parent

molecule to form toluene.

G. Data are given on some photochemical experiments designed to estimate E_a. Experimental difficulties (detailed in the text) prevented an assessment of this quantity.

H. A discussion of the results is given, and from the work with dibenzyl and deutero-dibenzyl it is concluded that of the conflicting literature values 45 k.cal./mole, and 69 k.cal./mole for the strength of the central C-C bond in dibenzyl, the former is to be preferred.

I. In order to obtain a numerical value for this bond energy from the pyrolysis of dibenzyl and the production of toluene, the following conditions would be necessary and are not satisfied in any of the work to date.

(a) The stoichiometry would have to be constant over all ranges of temperature and concentration.

(b) To obtain first order kinetics, an effective radical trap would have to be employed.

(c) If procedure (b) was not used then a reaction of order 1.5 would result and requires for interpretation that E_a be established in some fashion.

J. The method of following the rate of equilibration in mixtures of dibenzyl and deutero-dibenzyl developed in this work can be extended quantitatively to give the desired result. This is now being developed in St. Andrews by

I.M.T. Davidson.

Suggestions for Further Work

1. The use of equimolecular proportions of dibenzyl and deutero dibenzyl offers a promising line for following the rate of decomposition to benzyl radicals, provided a mass spectrometer of sufficient accuracy is available. Using an instrument with a resolution of 1 in 200, very small percentage decompositions could be detected accurately, and thus it should be possible, using a flow technique, and low temperatures, to determine the temperature dependence of the decomposition and hence the activation energy for the reaction

$$Ph.CH_2.CH_2.Ph \longrightarrow 2Ph.CH_2.$$

2. A static system could also be used to follow the decomposition over a considerable period of time. By constructing a reaction vessel having at its centre a mass spectrometer 'leak', the rate of growth of the 183^+ peak could be followed readily.

3. It would be worthwhile to repeat some of the kinetic work to determine the temperature dependence of toluene formation at higher partial pressures of dibenzyl so that a more satisfactory value of $E_{obs.}$ could be obtained. From this a value for E_a could then be calculated.

4. The pyrolysis of a compound of the type $Ph.CH_2.CHX.Ph$.

(where X. is Br., I., or some other group for which the C-X bond strength is less than 48 k.cal./mole.) would lead to a more detailed study of the reactions of the $Ph.CH_2.CH.Ph$ radical, and would throw some light on the secondary processes in the decomposition of dibenzyl.

APPENDIX A

Some Recent Evidence Relating to Dibenzyl

Graham, Nichol, & Ubbelhode, (62), working on the kinetics of Grignard reactions, have obtained a value for the substitution energy H - I in toluene.

$D(Ph.CH_2\text{-}H) - D(Ph.CH_2\text{-}I) = 34.3 \pm 1.3$ k.cal./mole.

If Szwarc's value is accepted for the bond dissociation energy in toluene, $D(Ph.CH_2\text{-}I)$ is found to be 43.2 ± 1.8 k.cal./mole. which agrees with the value of 43.7 k.cal./mole. obtained by Butler and Polanyi (63). If, however, the van Artsdalen value of 89.9 k.cal./mole. is substituted in the above expression, the value for $D(Ph.CH_2\text{-}I)$ becomes 55.6 k.cal./mole. This is therefore further evidence in favour of Szwarc's value of $D(Ph.CH_2\text{-}H) = 77.5$ k.cal./mole. and thus of $D(Ph.CH_2.CH_2.Ph) = 45$ k.cal./mole.

In the discussion of the fluorene experiments, it was stated that the results could be interpreted either by postulating a small but constant equilibrium concentration of benzyl radicals formed by the reaction

$$Ph.CH_2.CH_2.Ph \longleftrightarrow 2Ph.CH_2.$$

or by assuming that decomposition to benzyl radicals was complete or nearly complete at the temperature of the reaction vessel and that recombination and further re-

action occurred in the cooler outlet zone. The latter suggestion was discarded on the grounds that the presence of an equimolecular proportion of an effective radical acceptor such as fluorene would, under these conditions, result in a greater increase in toluene formation than was observed.

Loening, Ingold, & Henderson, (41), in experiments to determine the ionisation potential of the benzyl radical, pyrolysed benzyl iodide in a small retractable furnace in the head of a mass spectrometer. The observed products of this reaction were benzyl radicals with small quantities of dibenzyl and toluene. On racking the furnace away from the inlet to the ionisation chamber, it was found that the concentration of dibenzyl and benzyl in the analyser tube increased, but that of toluene remained constant. This is ample evidence that toluene was formed in the heated zone of the furnace, and did not occur by reaction outside the furnace in cooled portions of the flow system. Hence the rejection of the theory of complete dissociation is further justified.

The absence of hydrogen from the reaction products of dibenzyl has presented some difficulty in postulating a mechanism for the reaction. It should be noted, however, that Alexander, in some work as yet unpublished on the reaction between dibenzyl and iodine in the vapour phase, has

found that although hydrogen iodide was formed in considerable quantity, no trace of hydrogen could be found.

APPENDIX B

Thermochemical Calculations

The energy changes associated with chemical reactions can be calculated if the heats of formation of the reactants and resultants in the gas phase are known. Thus, for the reaction $Ph.CH_2.CH_2.Ph \longrightarrow 2.Ph.CH_2.$

$$\triangle H_f^{\circ}(Ph.CH_2CH_2.Ph)_{(g)} = 2.\triangle H_f^{\circ}(Ph.CH_2.)_{(g)} - D(Ph.CH_2.CH_2.Ph)$$

In this way the reaction energies quoted in the Discussion Section have been derived.

The heats of formation necessary for these calculations can be divided into two groups:- molecular and radical. Molecular values can be determined directly from their heats of combustion, together with latent heat data. The heat of formation of a radical cannot be derived in this way, but requires knowledge of the dissociation energies of a compound of the type R-X where the heat of formation of X is known.

The heats of formation of the following species are derived below.

Molecular	Radical
$Ph.CH_2.CH_2Ph$	$Ph.CH_2.$

Molecular	Radical
$Ph.CH_3$	$Ph.CH_2.CH_2.Ph$
$Ph.CH{=}CH.Ph$	$Ph.CH_2.CH_2.$
$Ph.H$	
$Ph.CH{=}CH_2$	

In the calculations the following heats of combustion have been used (68):-

$C_s + O_2 \longrightarrow CO_2(g) + 94.05$ k.cal.

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l) + 68.32$ k.cal.

Molecular Heats of Formation

Dibenzyl The heat of combustion in the solid state has been determined (67) as 1805.7 ± 0.3 k.cal./mole.

The heat of fusion is quoted as 5.64 k.cal./mole (72)

The vapour pressure over the liquid is quoted by D.P. Stull (69) as

mm Hg	1	5	10	20	40	60	100	200
°C	86.8	119.8	136	153.7	173.7	186	202.8	227.8

A plot of log p against $\frac{1}{T}$°K gives the latent heat of evaporation of 13.3 k.cal./mole.

Using these data we obtain

$14C_s + 7H_2 \longrightarrow C_4H_{14(g)} - 29.70$ k.cal.

i.e. $\Delta H_f^{\circ}(Ph.CH_2.CH_2.Ph) = 29.7$ k.cal./mole.

Toluene Data from American Petroleum Institute Project No.44 (70).

Heat of combustion of liquid toluene = 934.5 k.cal.

Heat of vaporisation = 9.08 k.cals.

$\therefore 7C_s + 4H_2 \longrightarrow C_7H_{8(g)} - 11.95$

$\triangle H_f^\circ(Ph.CH_3) = 11.95$ k.cal./mole.

Stilbene Heat of combustion of solid = 1758.8 k.cals.(71)

Heat of fusion = 7.18 k.cal./mole.(72)

The vapour pressure over liquid stilbene (trans) is given (69) as:-

mm Hg	1	5	10	20	40	60	100	200
°C	113.2	145.8	161.	179.8	199	211.5	227.4	251.7

A plot log p against $\frac{1}{T}$° K gives the heat of evaporation as 14.95 k.cal./mole.

Therefore $14C_s + 6H_2 \longrightarrow C_{14}H_{12(g)} - 54.31$

i.e. $\triangle H_f^\circ(Ph.CH{=}CH.Ph) = 54.31$ k.cal./mole.

Benzene Data from American Petroleum Institute Project 44 (70).

Heat of combustion of liquid = 780.98 k.cal./mole.

Heat of vaporisation = 8.09 k.cal./mole.

Therefore $6C_s + 3H_2 \longrightarrow C_6H_{6(g)} - 19.82$

$\triangle H_f^\circ(Ph.H) = 19.82$ k.cal./mole.

Styrene Data from American Petroleum Institute Project 44 (70).

Heat of combustion of liquid = 954.50 k.cal./mole.

Heat of vaporisation = 10.39 k.cal./mole.

Therefore $8C_s + 4H_2 \longrightarrow C_8H_{8(g)} - 35.11$

i.e. $\triangle H_f^\circ(Ph.CH{=}CH_2) = 35.11$ k.cal./mole.

Radical Heats of Formation

1. The Benzyl Radical $Ph.CH_2\cdot$

The methods applied above for molecular heats of formation cannot be used to determine the $\triangle H_f^\circ$ values for radicals since radical heats of combustion cannot be obtained directly. It is therefore necessary to utilise the measured heat of dissociation of a molecule of the type $Ph.CH_2$-X where $\triangle H_f^\circ(X)$ is known.

Since there are two conflicting values for $D(Ph.CH_2\text{-}H)$(see page 38) two values of $\triangle H_f^\circ(Ph.CH_2\cdot)$ are possible.

$$Ph.CH_3 \longrightarrow Ph.CH_2\cdot + H\cdot - D(Ph.CH_2\text{-}H)$$

$$\triangle H_f^\circ(Ph.CH_3) = \triangle H_f^\circ(Ph.CH_2\cdot) + \triangle H_f^\circ(H.) - D(Ph.CH_2\text{-}H)$$

now $H_2 \longrightarrow 2H\cdot = 104$ k.cal./mole.

$\therefore \triangle H_f^\circ(H.) = 52$.k.cal./mole.

$\therefore \triangle H_f^\circ(Ph.CH_2\cdot) = 11.95 - 52 + D(Ph.CH_2\text{-}H)$

If the Szwarc value of 77.5 k.cal./mole. is assumed for $D(Ph.CH_2\text{-}H)$

$$\triangle H_f^\circ(Ph.CH_2\cdot) = 37.45 \text{ k.cal./mole.}$$

If however 89.5 k.cal./mole. is used

$$\triangle H_f^\circ(Ph.CH_2\cdot) = 49.45 \text{ k.cal./mole.}$$

2. $Ph.CH_2.CH.Ph$

$$Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH_2CH.Ph + H - D(Ph.CH_2.CH\text{-}H.Ph)$$

The dissociation energy of the C-H bond in dibenzyl has not been determined, so for these calculations a rough estimate is made. Since this is a secondary bond,

it would be expected to have a value a few k.cals. less than for the C-H bond in the side chain of toluene. Since the difference between primary and secondary C-H bonds is roughly 7 k.cal./mole., an approximate value of 70.5 k.cal./mole. has been assumed for further calculations.

$$\triangle H_f^\circ(Ph.CH_2.CH_2.Ph) = \triangle H_f^\circ(Ph.CH_2.CH.Ph) + \triangle H_f^\circ(H.) - D(Ph.CH_2.CH-H.Ph)$$

$$\therefore \triangle H_f^\circ(Ph.CH_2.CH.Ph) = 29.7 - 52.0 + 70.5$$

$$= 48.2 \text{ k.cal./mole.}$$

3. $Ph.CH_2.CH_2.$

This value also cannot be determined directly as compounds of the type $Ph.CH_2.CH_2.X$ give as decomposition products the radicals $Ph.CH_2.$ and $X.CH_2.$, not $Ph.CH_2.CH_2.$ and X.

However if it is assumed that $D(Ph.CH_2.CH_2-H)$ is similar to $D(CH_3.CH_2-H)$ a value for the heat of formation of the radical can be obtained.

$D(CH_3.CH_2-H) = 96$ k.cal./mole.(73) $\approx D(Ph.CH_2.CH_2.-H)$

$$Ph.CH_2.CH_3 \longrightarrow Ph.CH_2.CH_2. + H$$

$$\triangle H_f^\circ(Ph.CH_2.CH_3) = \triangle H_f^\circ(Ph.CH_2.CH_2.) + \triangle H_f^\circ(H.) - D(Ph.CH_2.CH_2-H)$$

$\triangle H_f^\circ(Ph.CH_2.CH_3) = 7.12$ k.cal./mole. (70)

$\therefore \triangle H_f^\circ(Ph.CH_2.CH_2.) = 51$ k.cal./mole. (approximately)

4. Ph.

Calculations for the value of $\triangle H_f^\circ(Ph.)$ from the data

available in the literature vary widely depending on the sources used. For example, Cowan (53) studied the thermal decomposition of phenyl iodide and obtained D(Ph-I) = 60.7 k.cal./mole. With this and the heat of combustion of phenyl iodide claimed by Berthelot (74) he calculated $\triangle H_f^\circ$(Ph.) = 78.2 k.cal./mole. If, however, Szwarc's value of D(Ph-Br) = 71 k.cal./mole (75) is used in conjunction with $\triangle H_{f(l)}^c$(Ph.Br) = 8.8 k.cal./mole and a heat of evaporation of 9.1 k.cal./mole (78) a value of 62.2 k. cal./mole. can be calculated for the heat of formation of the phenyl radical.

Skinner et al. (77) have reviewed the available data and have concluded that $\triangle H_f^\circ$(Ph.) = 69±4 k.cal./mole. This is supported by work on the pyrolysis of diphenylmethane (52) when the initial reactions proved to be

$$Ph.CH_2.Ph \longrightarrow Ph.CH.Ph + H. \qquad 1.$$

and there was no evidence of the reaction

$$Ph.CH_2.Ph \longrightarrow Ph.CH_2. + Ph. \qquad 2.$$

The dissociation energy of process 1. was found to be 73 k.cal./mole. and so if we assume similar temperature independent factors for 1. and 2., the dissociation energy of the latter must be greater than 73 k.cal/mole. Thus for reaction 2.

$$\triangle H_f^\circ(Ph.CH_2.Ph) = \triangle H_f^\circ(Ph.CH_2.) + \triangle H_f^\circ(Ph.) - D(Ph - CH_2.Ph)$$

$33.2\ (70) = 37.5 + \triangle H_f^\circ(Ph.) - > 73$

i.e. $\triangle H_f^\circ(Ph.) > 68.7$

As an accurate value is not essential for the Discussion, $\triangle H_f^\circ(Ph.) = 69$ k.cal./mole. has been assumed.

Heats of Reaction

With these values the energy changes in the proposed reactions can be determined.

The Initial Process

$Ph.CH_2.CH_2.Ph. \longrightarrow 2Ph.CH_2. - D(Ph.CH_2-CH_2.Ph)$

$\triangle H_f^\circ(Ph.CH_2.CH_2.Ph) = 2\triangle H_f^\circ(Ph.CH_2.) - D(Ph.CH_2-CH_2.Ph)$

For $\triangle H_f^\circ(Ph.CH_2.) = 37.45$ k.cal./mole.

$D(Ph.CH_2-CH_2.Ph) = 2 \times 37.45 - 29.7$

$= 45.2$ k.cal./mole.

For $\triangle H_f^\circ(Ph.CH_2.) = 49.45$ k.cal./mole.

$D(Ph.CH_2-CH_2.Ph) = 69.2$ k.cal./mole.

The Subsidiary Reactions

These are taken in the order in which they appear in the Discussion (pages 138 to 142) and have the same lettering. As the evidence put forward in this thesis is in favour of a value of 45 k.cal./mole. for $D(Ph.CH_2-CH_2.Ph)$ $\triangle H_f^\circ(Ph.CH_2.) = 37.45$ k.cal./mole. has been used in all subsequent calculations.

(a) $Ph.CH_2. + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH_3 + Ph.CH_2.CH.Ph$

$\triangle H^\circ$ reaction $= 11.95 + 48.2 - 37.45 - 29.7$

$= -7.0$ k.cal./mole.

(b) $Ph.CH.CH_2.Ph \longrightarrow Ph.CH = CH.Ph + H.$

$\triangle H^\circ$ reaction = 54.31 + 52 - 48.2

= 58.11 k.cal./mole.

(c) $H. + Ph.CH_2.CH_2.Ph \longrightarrow Ph.H + Ph.CH_2.CH_2.$

$\triangle H^\circ$ reaction = 19.81 + 51. - 52. - 29.70

= -10.89 k.cal./mole.

(d) $Ph.CH_2.CH_2. \longrightarrow Ph.CH=CH_2 + H.$

$\triangle H^\circ$ reaction = 35.11 + 52 - 51

= 36.11 k.cal./mole.

(e) $Ph.CH.CH_2.Ph \longrightarrow Ph.CH=CH_2 + Ph.$

$\triangle H^\circ$ reaction = 35.11 + 69 - 37.45

= 66.66 k.cal./mole.

(f) $Ph.CH_2.CH_2.Ph + Ph. \longrightarrow Ph.H + Ph.CH.CH_2.Ph.$

$\triangle H^\circ$ reaction = 19.81 + 48.2 - 29.7 - 69

= -30.69 k.cal./mole.

(g) $2\,Ph.CH.CH_2.Ph \longrightarrow Ph.CH=CH.Ph + Ph.CH_2.CH_2.Ph$

$\triangle H^\circ$ reaction = 54.31 + 29.70 - 96.4

= -12.39 k.cal./mole.

(h) $H + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH.CH_2.Ph + H_2$

$\triangle H^\circ$ reaction = 48.2 - 52 - 29.7

= -33.5 k.cal./mole.

(i) $H + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH_3 + Ph.CH_2.$

$\triangle H^\circ$ reaction = 11.95 + 37.45 - 52 - 29.7

= -32.3. k.cal./mole.

(k) $Ph.CH.CH_2.Ph + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH{=}CH.Ph + Ph.CH_3 + Ph.CH_2\cdot$

$\triangle H^\circ$ reaction = 54.31 + 11.95 + 37.45 - 48.2 - 29.7

= 25.81 k.cal./mole.

(l) $Ph.CH.CH_2.Ph + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH{=}CH.Ph + Ph.H + Ph.CH_2.CH_2\cdot$

$\triangle H^\circ$ reaction = 54.31 + 19.81 + 51 - 48.2 - 29.7

= 47.22 k.cal./mole.

(m) $Ph.CH_2.CH_2\cdot + Ph.CH_2.CH_2.Ph \longrightarrow Ph.CH{=}CH_2 + Ph.CH_3 + Ph.CH_2\cdot$

$\triangle H^\circ$ reaction = 35.11 + 11.95 + 37.45 - 51 - 29.7

= 3.81 k.cal./mole.

APPENDIX C

Detailed Experimental Results

Table 7.

Dibenzyl alone. Effect of temperature.

No.	Temp. °K	Contact Time(sec)	p.p.(m.m.) Dibenzyl	p.p.(m.m.) Nitrogen	Concentration (moles/l.x 10^8)					$(\times 10^2)$ $k_{uni.}$	$K_{1.5}$
					Dibenzyl	Styrene	Toluene	Benzene	Stilbene		
30	908	0.218	0.278	4.93	491	2.57	3.83	1.84	0.912	1.88	8.05
31	906	0.218	0.291	4.94	515	1.73	3.14	1.09	0.918	1.51	6.42
32	906	0.219	0.255	5.00	451	1.37	2.76	0.736	0.899	1.45	6.69
33	857	0.238	0.268	4.58	501	0.427	0.914	0.252	0.557	0.392	1.68
34	859	0.237	0.266	4.59	496	0.326	0.720	0.215	0.496	0.351	1.36
35	857	0.239	0.241	4.61	451	0.256	0.637	0.137	0.532	0.307	1.49
39	986	0.218	0.232	4.44	377	13.3	26.4	5.13	2.46	17.3	84.7
40	989	0.209	0.378	4.29	599	11.8	27.0	4.36	2.83	11.9	46.5
41	989	0.205	0.384	4.43	622.	12.1	27.9	4.38	3.32	11.4	44.9

Table 8

Dibenzyl alone. Effect of partial pressure changes

No.	Temp. °K	Contact Time (Sec)	p.p. (m.m.) Dibenzyl	p.p. (m.m.) Nitrogen	Concentration (moles/l. x 10^8)					$(x10^2)$ $k_{uni.}$
					Dibenzyl	Styrene	Toluene	Benzene	Stilbene	
50	959	0.206	0.164	6.00	275	6.75	15.8	2.62	1.13	13.3
51	959	0.200	0.258	5.99	431	6.46	15.9	2.83	1.72	8.88
52	959	0.197	0.252	6.04	422	6.30	16.3	2.89	1.50	9.52
60	963	0.291	0.277	2.69	464	5.53	17.1	2.73	3.06	6.17
61	964	0.281	0.300	2.81	500	6.49	19.8	2.92	3.42	6.84
62	963	0.270	0.307	2.94	511	6.54	20.8	2.92	3.61	7.30
63	967	0.305	0.262	2.63	434	6.77	22.1	2.62	2.97	7.78
64	968	0.294	0.320	2.65	530	5.91	20.3	2.62	4.11	6.38
65	969	0.292	0.288	2.74	478	5.49	20.2	2.34	3.16	7.05
66	956	0.242	0.240	3.43	404	3.09	12.0	2.09	1.90	6.00
67	956	0.241	0.254	3.88	434	3.37	11.2	1.82	2.08	5.27
68	957	0.239	0.276	3.88	447	3.18	12.7	2.06	2.06	5.78
69	966	0.203	0.330	9.39	548	4.21	16.2	3.20	3.34	7.00
70	966	0.200	0.401	9.24	667	4.60	16.3	2.86	4.15	6.01
71	965	0.202	0.396	9.26	660	4.87	17.6	2.76	3.92	6.38
72	968	0.235	0.181	4.13	300	2.24	7.78	1.22	1.37	5.37
73	968	0.234	0.178	4.14	295	2.24	8.35	1.21	1.41	5.98
74	968	0.233	0.177	4.16	294	2.30	8.79	1.05	1.40	6.27

Table 9

Dibenzyl and Fluorene. Variation of fluorene concentration

No.	Temp. °K.	Contact Time(sec)	p.p.(m.m.) Dibenzyl	p.p.(m.m.) Fluorene	p.p.(m.m.) Nitrogen	Concentration (moles/l.x 10^8)					$(x10^2)$ $k_{uni.}$
						Styrene	Toluene	Benzene	Dibenzyl	Fluorene	
103	906	0.212	0.217	0.388	4.09	1.23	22.4	0.83	370	659.	13.4
104	906	0.211	0.217	0.386	4.10	1.20	20.0	0.77	360	640.	13.5
105	906	0.211	0.217	0.387	4.10	1.13	20.4	0.72	360	640.	13.5
106	908	0.205	0.212	0.567	3.80	0.90	26.4	0.71	350	935.	17.3
107	908	0.205	0.212	0.566	3.79	1.09	26.9	0.81	350	935	20.9
108	908	0.205	0.212	0.566	3.79	0.96	25.3	0.28	350	935	17.3
109	908	0.208	0.215	0.499	3.76	0.98	30.2	0.47	355	825	20.6
110	911	0.207	0.214	0.498	3.76	0.97	30.8	0.62	354	823	20.7
111	911	0.207	0.215	0.499	3.76	0.86	27.4	0.54	354	823	19.3
112	910	0.208	0.215	0.498	4.15	1.16	19.1	0.75	355	821	11.4
113	910	0.205	0.212	0.491	4.17	1.71	27.8	0.68	350	809	19.5
114	910	0.205	0.212	0.490	4.16	1.71	22.6	0.74	350	809	15.9
115	907	0.174	0.179	1.28	3.15	0.73	42.5	0.94	298	2120	29.3
116	910	0.172	0.178	1.27	3.13	0.72	43.5	0.78	294.	2095	44.7
117	911	0.172	0.179	1.28	3.11	1.00	42.3	0.78	294	2095	30.5
118	906	0.231	0.239	0.087	4.28	0.78	5.14	1.23	394	145.	2.80
119	909	0.255	0.264	0.081	4.25	1.12	6.55	2.07	436.	134.	2.93
120	908	0.239	0.247	0.090	4.29	0.86	5.65	1.58	408	149.	2.92

Table 9. (continued)

No.	Temp. °K.	Contact Time(sec)	p.p.(m.m.) Dibenzyl	p.p.(m.m.) Fluorene	p.p.(m.m.) Nitrogen	Concentration (moles/l.x 10^8)					$(x10^2)$ $k_{uni.}$
						Styrene	Toluene	Benzene	Dibenzyl	Fluorene	
121	907	0.237	0.245	0.087	4.33	0.85	5.58	1.48	405	144.	2.94
122	906	0.234	0.241	0.096	4.03	0.84	6.10	1.59	400	159	3.33
123	906	0.237	0.244	0.102	4.11	0.80	6.07	1.87	405	169	3.15
124	906	0.258	0.266	0.106	4.07	0.87	6.24	1.62	440	175	2.74
125	906	0.228	0.235	0.132	4.16	1.25	6.18	0.94	390	185	3.46
126	906	0.225	0.232	0.148	4.14	1.23	7.29	0.89	385	246.	4.20
127	905	0.227	0.234	0.144	4.15	1.24	7.70	0.87	388	238	4.38
128	906	0.224	0.231	0.175	4.32	1.22	8.58	1.02	383	289	5.02
129	906	0.225	0.232	0.197	4.28	1.30	9.24	0.88	384	326	5.38
130	907	0.226	0.233	0.189	4.29	1.16	9.05	1.08	386	313	5.24
131	907	0.218	0.226	0.310	4.13	0.83	11.6	0.84	373	512	7.19
132	908	0.218	0.225	0.306	4.14	1.16	11.8	0.73	373	506	7.19
133	908	0.216	0.223	0.301	4.17	0.99	11.6	0.96	370	500	7.26
134	908	0.214	0.221	0.374	4.05	0.98	14.9	0.74	366	620	9.58
135	908	0.213	0.220	0.394	3.97	1.05	14.6	0.68	364	635	9.48
136	907	0.215	0.222	0.387	3.97	1.06	14.9	0.83	368	641	9.53
143	905	0.151	0.155	1.69	2.66	0.43	31.6	0.73	264	2880.	40.7
144	905	0.151	0.156	1.62	2.71	0.43	32.3	0.88	266	2760	41.6

Table 10

Dibenzyl alone. Effect of partial pressure variations: injection system

No.	Temp. °K.	Contact Time(sec)	p.p.(m.m.) Dibenzyl	p.p.(m.m.) Nitrogen	Concnetration (moles/l.x 10^9)					$k_{1.5}$
					Dibenzyl	Styrene	Toluene	Benzene	Stilbene	
146	906	0.265	0.269	4.15	482	2.21	4.51	1.60	1.30	26.0
147	905	0.251	0.336	3.98	597	2.67	4.87	1.31	1.95	20.8
148	904	0.250	0.335	4.01	587	2.32	4.16	1.08	1.73	18.9
149	906	0.252	0.298	4.06	519	2.05	4.17	0.99	1.83	22.5
150	904	0.269	0.142	4.08	257	0.63	1.59	0.32	0.70	22.9
151	904	0.267	0.130	4.09	238	0.67	1.50	0.31	0.70	22.7
152	904	0.268	0.141	4.08	247	0.68	1.54	0.30	0.69	24.6
153	904	0.274	0.087	4.23	153	0.31	0.75	0.19	0.42	25.1
154	904	0.277	0.085	420	150	0.30	0.75	0.18	0.43	24.6
155	904	0.275	0.085	4.21	150	0.26	0.80	0.16	0.43	24.8
157	904	0.225	0.790	3.47	1400	10.0	15.2	7.57	7.08	21.7
158	904	0.223	0.816	3.45	1440	10.8	16.1	8.30	7.98	20.6
159	904	0.221	0.850	3.49	1510	11.0	16.7	8.87	8.01	19.3
189	904	0.256	0.497	3.87	882	5.30	8.80	3.92	3.19	21.0
190	904	0.255	0.503	3.88	894	4.99	8.62	3.67	3.25	20.1
191	904	0.252	0.500	3.90	888	4.98	9.37	3.68	3.26	22.4
192	904	0.221	0.913	3.50	1620	11.4	18.1	7.85	7.50	20.2

Table 10 (continued)

No.	Temp. °K.	Contact Time (sec)	p.p. (m.m.) Dibenzyl	p.p. (m.m.) Nitrogen	Concentration (moles/l. x 10^9)					$k_{1.5}$
					Dibenzyl	Styrene	Toluene	Benzene	Stilbene	
193	904	0.227	0.825	3.61	1460	10.6	16.2	7.14	6.78	20.0
194	904	0.230	0.775	3.70	1370	8.74	14.5	6.30	6.33	19.0
198	904	0.219	1.054	3.35	1870	15.7	20.0	12.4	10.2	17.7
199	904	0.223	0.977	3.47	1730	13.8	18.1	11.4	10.6	18.2
200	904	0.216	1.008	3.46	1790	11.9	15.8	10.4	10.2	15.6
201	904	0.229	0.941	3.49	1670	11.7	15.5	9.38	7.48	16.4
202	904	0.229	0.909	3.59	1640	12.0	15.8	9.52	8.09	16.6
203	904	0.224	0.934	3.63	1660	11.9	15.6	9.39	8.10	16.7

Table 11

Dibenzyl alone. Effect of temperature at a lower partial pressure.

No.	Temp. °K	Contact Time(sec)	p.p.(m.m.) Dibenzyl	p.p.(m.m.) Nitrogen	Concentration (moles/l.x 10^8)					$k_{1.5}$
					Dibenzyl	Styrene	Toluene	Benzene	Stilbene	
268	895	0.238	0.163	3.37	248	0.624	2.24	0.697	0.948	11.76
269	896	0.235	0.185	3.26	276	0.724	2.49	0.807	0.986	12.12
270	868	0.246	0.153	3.31	235	0.366	1.24	0.701	0.601	7.00
271	869	0.244	0.165	3.06	237	0.375	1.23	0.621	0.561	6.96
272	868	0.243	0.165	3.05	235	0.382	1.32	0.615	0.583	7.55
273	957	0.219	0.213	3.24	291	1.98	10.1	1.40	2.31	47.05
274	957	0.217	0.229	3.14	309	2.19	11.8	2.06	2.52	50.77
275	957	0.218	0.223	3.16	302	2.98	12.3	1.80	2.52	54.57
276	825	0.258	0.153	3.30	244	0.149	0.353	0.320	0.784	1.72
277	830	0.256	0.160	3.23	252	0.162	0.442	0.315	0.960	2.14
278	835	0.255	0.157	3.28	248	0.204	0.532	0.384	0.956	2.72

Table 12

Dibenzyl Alone. Photochemical Experiments.

No.	Temp. °K.	Contact Time(sec)	p.p.(m.m.) Dibenzyl	p.p.(m.m.) Nitrogen	Concentration moles/l			Rate(Tol.) Moles/l/ ($\times 10^{10}$)sec.
					Dibenzyl($\times 10^{6}$)	Toluene($\times 10^{10}$)	Benzene($\times 10^{10}$)	
249	534	0.593	0.150	3.91	4.48	6.86	3.33	11.6
250	534	0.606	0.154	3.85	4.63	6.04	2.91	10.0
251	534	0.593	0.169	3.84	5.07	5.62	3.08	9.48
253	578	0.550	0.164	3.93	4.54	6.04	4.86	11.0
254	580	0.544	0.166	3.91	4.59	3.64	6.87	6.69
255	578	0.558	0.160	3.88	4.45	3.73	3.70	6.68
256	574	0.570	0.179	3.95	5.00	6.72	12.3	11.8
257	574	0.570	0.174	3.89	4.87	4.64	12.6	8.14
258	572	0.568	0.166	3.88	4.65	3.89	12.6	6.85
259	491	0.656	0.237	3.78	7.71	6.22	5.34	9.48
260	493	0.652	0.297	3.68	9.62	4.05	4.32	6.21
261	494	0.642	0.326	3.66	10.6	3.99	5.00	6.21

APPENDIX D

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